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(54) Title: NONIONIC SURFACTANT SYSTEMS CONTAINING POLYHYDROXY FATTY ACID AMIDES AND ONE OR MORE ADDITIONAL NONIONIC SURFACTANTS			
$\text{R}^2 - \overset{\overset{\text{O}}{\parallel}}{\text{C}} - \overset{\overset{\text{R}^1}{ }}{\text{N}} - \text{Z} \quad (\text{I})$			
(57) Abstract <p>The present invention provides nonionic surfactant systems comprising: (a) one or more polyhydroxy fatty acid amides having formula (I), wherein R¹ is H, a C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or mixtures thereof, R² is a C₅-C₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least three hydroxyl groups directly connected to the chain, or an alkoxyated derivative thereof; and (b) one or more additional nonionic surfactants; wherein the weight ratio of polyhydroxy fatty acid amide (a) to additional nonionic surfactant (b) is in the range of from about 1:5 to about 5:1. The present invention also provides laundry detergent compositions which contain the nonionic surfactant systems described above. When included in such laundry detergent compositions, these nonionic surfactant systems unexpectedly improve the stain removal performance of such compositions against greasy/oily stains across a broad range of laundry conditions. This invention further provides a method for improving the stain-removing performance of detergent compositions by incorporating into such compositions the nonionic surfactant systems described above.</p>			

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NONIONIC SURFACTANT SYSTEMS CONTAINING POLYHYDROXY FATTY ACID
AMIDES AND ONE OR MORE ADDITIONAL NONIONIC SURFACTANTS

5 FIELD OF INVENTION

The stain-removing performance of detergent compositions is improved through the use of a nonionic surfactant system comprising one or more polyhydroxy fatty acid amides and one or more additional nonionic surfactants.

10

15 BACKGROUND OF INVENTION

Conventional laundry detergent compositions can be formulated in a number of different ways to address a number of different laundering problems. For example, such detergent compositions may contain builders, optical brighteners, dispersants, etc., to address various cleaning problems encountered in laundering operations. Furthermore, consumers need detergent compositions which are effective against the broadest possible spectrum of stains and soils. Detergent formulators address this need by providing detergent compositions containing mixed surfactants which are broadly effective in their cleaning performance.

25

One particular problem which must be considered and addressed when formulating detergent compositions is the removal of troublesome greasy/oily stains, such as body soils, food soils, etc. The inclusion of nonionic surfactants in laundry detergent compositions will improve the effectiveness of such compositions against greasy/oily stains, but only under limited laundry conditions.

30

The present invention provides nonionic surfactant systems which comprise one or more polyhydroxy fatty acid amides and one or more additional nonionic surfactants. The present invention also provides laundry detergent compositions which contain these nonionic surfactant systems. When included in such laundry detergent compositions, these nonionic surfactant systems unexpectedly improve the effectiveness of such compositions against greasy/oily stains across a broad range of laundry conditions.

35

BACKGROUND ART

5 A variety of polyhydroxy fatty acid amides have been described in the art. N-acyl, N-methyl glucamides, for example, are disclosed by J. W. Goodby, M. A. Marcus, E. Chin, and P. L. Finn in "The Thermotropic Liquid-Crystalline Properties of Some
10 Straight Chain Carbohydrate Amphiphiles," Liquid Crystals, 1988, Volume 3, No. 11, pp 1569-1581, and by A. Muller-Fahrnow, V. Zabel, M. Steifa, and R. Hilgenfeld in "Molecular and Crystal Structure of a Nonionic Detergent: Nonanoyl-N-methylglucamide," J. Chem. Soc. Chem. Commun., 1986, pp 1573-1574. The use of N-alkyl polyhydroxyamide surfactants has been of substantial interest recently for use in biochemistry, for example in the dissociation of biological membranes. See, for example, the journal article
15 "N-D-Gluco-N-methyl-alkanamide Compounds, a New Class of Non-Ionic Detergents For Membrane Biochemistry," Biochem. J. (1982), Vol. 207, pp 363-366, by J. E. K. Hildreth.

The use of N-alkyl glucamides in detergent compositions has also been discussed. U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and G.B. Patent 809,060, published February
20 18, 1959, assigned to Thomas Hedley & Co., Ltd. relate to detergent compositions containing anionic surfactants and certain amide surfactants, which can include N-methyl glucamide, added as a low temperature suds enhancing agent. These compounds include an N-acyl radical of a higher straight chain fatty acid having 10-14
25 carbon atoms. These compositions may also contain auxiliary materials such as alkali metal phosphates, alkali metal silicates, sulfates, and carbonates. It is also generally indicated that additional constituents to impart desirable properties to the composition can also be included in the compositions, such as
30 fluorescent dyes, bleaching agents, perfumes, etc.

U.S. Patent 2,703,798, issued March 8, 1955 to A. M. Schwartz, relates to aqueous detergent compositions containing the condensation reaction product of N-alkyl glucamine and an ali-
35 phatic ester of a fatty acid. The product of this reaction is said to be useable in aqueous detergent compositions without further purification. It is also known to prepare a sulfuric ester of acylated glucamine as disclosed in U.S. Patent 2,717,894, issued September 13, 1955, to A. M. Schwartz.

- 3 -

PCT International Application WO 83/04412, published December 22, 1983, by J. Hildreth, relates to amphiphilic compounds containing polyhydroxyl aliphatic groups said to be useful for a variety of purposes including use as surfactants in cosmetics, drugs, shampoos, lotions, and eye ointments, as emulsifiers and dispensing agents for medicines, and in biochemistry for solubilizing membranes, whole cells, or other tissue samples, and for preparing of liposomes. Included in this disclosure are compounds of the formula $R'CON(R)CH_2R''$ and $R''CON(R)R'$ wherein R is hydrogen or an organic grouping, R' is an aliphatic hydrocarbon group of at least three carbon atoms, and R'' is the residue of an aldose.

European Patent 0 285 768, published October 12, 1988, H. Kelkenberg, et al., relates to the use of N-polyhydroxy alkyl fatty acid amides as thickening agents in aqueous detergent systems. Included are amides of the formula $R_1C(O)N(X)R_2$ wherein R_1 is a C_1 - C_{17} (preferably C_7 - C_{17}) alkyl, R_2 is hydrogen, a C_1 - C_{18} (preferably C_1 - C_6) alkyl, or an alkylene oxide, and X is a polyhydroxy alkyl having four to seven carbon atoms, e.g., N-methyl, coconut fatty acid glucamide. The thickening properties of the amides are indicated as being of particular use in liquid surfactant systems containing paraffin sulfonate, although the aqueous surfactant systems can contain other anionic surfactants, such as alkylaryl sulfonates, olefin sulfonate, sulfosuccinic acid half ester salts, and fatty alcohol ether sulfonates, and nonionic surfactants such as fatty alcohol polyglycol ether, alkylphenol polyglycol ether, fatty acid polyglycol ester, polypropylene oxide-polyethylene oxide mixed polymers, etc. Paraffin sulfonate/N-methyl coconut fatty acid glucamide/nonionic surfactant shampoo formulations are exemplified. In addition to thickening attributes, the N-polyhydroxy alkyl fatty acid amides are said to have superior skin tolerance attributes.

U.S. Patent 2,982,737, issued May 2, 1961, to Boettner, et al., relates to detergent bars containing urea, sodium lauryl sulfate anionic surfactant, and an N-alkylglucamide nonionic surfactant which is selected from N-methyl, N-sorbityl lauramide and N-methyl, N-sorbityl myristamide.

Other glucamide surfactants are disclosed, for example, in DT 2,226,872, published December 20, 1973, H. W. Eckert, et al., which relates to washing compositions comprising one or more surfactants and builder salts selected from polymeric phosphates, sequestering agents, and washing alkalis, improved by the addition of an N-acylpolyhydroxyalkyl-amine of the formula $R_1C(O)N(R_2)CH_2-(CHOH)_nCH_2OH$, wherein R_1 is a C_1 - C_3 alkyl, R_2 is a C_{10} - C_{22} alkyl, and n is 3 or 4. The N-acylpolyhydroxyalkyl-amine is added as a soil suspending agent.

U.S. Patent 3,654,166, issued April 4, 1972, to H. W. Eckert, et al., relates to detergent compositions comprising at least one surfactant selected from the group of anionic, zwitterionic, and nonionic surfactants and, as a textile softener, an N-acyl, N-alkyl polyhydroxylalkyl compound of the formula $R_1N(Z)C(O)R_2$ wherein R_1 is a C_{10} - C_{22} alkyl, R_2 is a C_7 - C_{21} alkyl, R_1 and R_2 total from 23 to 39 carbon atoms, and Z is a polyhydroxyalkyl which can be $-CH_2(CHOH)_mCH_2OH$ where m is 3 or 4.

U.S. Patent 4,021,539, issued May 3, 1977, to H. Möller, et al., relates to skin treating cosmetic compositions containing N-polyhydroxylalkyl-amines which include compounds of the formula $R_1N(R)CH(CHOH)_mR_2$ wherein R_1 is H, lower alkyl, hydroxy-lower alkyl, or aminoalkyl, as well as heterocyclic aminoalkyl, R is the same as R_1 but both cannot be H, and R_2 is CH_2OH or $COOH$.

French Patent 1,360,018, April 26, 1963, assigned to Commercial Solvents Corporation, relates to solutions of formaldehyde stabilized against polymerization with the addition of amides of the formula $RC(O)N(R_1)G$ wherein R is a carboxylic acid functionality having at least seven carbon atoms, R_1 is hydrogen or a lower alkyl group, and G is a glycitol radical with at least 5 carbon atoms.

German Patent 1,261,861, February 29, 1968, A. Heins, relates to glucamine derivatives useful as wetting and dispersing agents of the formula $N(R)(R_1)(R_2)$ wherein R is a sugar residue of glucamine, R_1 is a C_{10} - C_{20} alkyl radical, and R_2 is a C_1 - C_5 acyl radical.

G.B. Patent 745,036, published February 15, 1956, assigned to Atlas Powder Company, relates to heterocyclic amides and carboxylic esters thereof that are said to be useful as chemical

- 5 -

intermediates, emulsifiers, wetting and dispersing agents, detergents, textile softeners, etc. The compounds are expressed by the formula $N(R)(R_1)C(O)R_2$ wherein R is the residue of an anhydri-
 5 zed hexane pentol or a carboxylic acid ester thereof, R_1 is a mono-valent hydrocarbon radical, and $-C(O)R_2$ is the acyl radical of a carboxylic acid having from 2 to 25 carbon atoms.

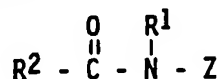
U.S. Patent 3,312,627, issued April 4, 1967 to D. T. Hooker, discloses solid toilet bars that are substantially free of anionic
 10 detergents and alkaline builder materials, and which contain lithium soap of certain fatty acids, a nonionic surfactant selected from certain propylene oxide-ethylenediamine-ethylene oxide condensates, propylene oxide-propylene glycol-ethylene oxide condensates, and polymerized ethylene glycol, and also contain a nonionic lathering component which can include polyhydroxyamide of
 15 the formula $RC(O)NR^1(R^2)$ wherein $RC(O)$ contains from about 10 to about 14 carbon atoms, and R^1 and R^2 each are H or C_1 - C_6 alkyl groups, said alkyl groups containing a total number of carbon atoms of from 2 to about 7 and a total number of substituent hydroxyl groups of from 2 to about 6. A substantially similar
 20 disclosure is found in U.S. Patent 3,312,626, also issued April 4, 1967 to D. T. Hooker.

The use of nonionic surfactants in detergent compositions is known in the art. U.S. Patent 3,654,166, issued April 4, 1972 to Eckert et al., discloses detergent compositions comprising a
 25 surfactant selected from anionics, zwitterionics and nonionics and an N-alkyl-N-acyl-N-polyhydroxyalkyl compound.

SUMMARY OF THE INVENTION

The present invention is directed to nonionic surfactant systems comprising:

- 30 (a) one or more polyhydroxy fatty acid amides having the formula



wherein R^1 is H, a C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or mixtures thereof, R^2 is a C_5 - C_{31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a
 35 linear hydrocarbyl chain with at least 3 hydroxyl groups

- 6 -

directly connected to the chain, or an alkoxyated derivative thereof; and

(b) one or more additional nonionic surfactants;

5 wherein the weight ratio of polyhydroxy fatty acid amide (a) to additional nonionic surfactant (b) is in the range of from about 1:5 to about 5:1.

10 The present invention also provides laundry detergent compositions which contain the nonionic surfactant systems described above. When included in such laundry detergent compositions, these nonionic surfactant systems unexpectedly improve the stain removal performance of such compositions against greasy/oily stains across a broad range of laundry conditions.

15 This invention further provides a method for improving the stain-removing performance of detergent compositions by incorporating into such compositions the nonionic surfactant systems described above.

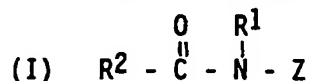
DETAILED DESCRIPTION OF THE INVENTION

20 The nonionic surfactant systems of the present invention comprise one or more polyhydroxy fatty acid amides and one or more additional nonionic surfactants. In these nonionic surfactant systems the weight ratio of polyhydroxy fatty acid amides to additional nonionic surfactants is in the range of from about 1:5 to about 5:1, preferably from about 1:3 to about 3:1, more preferably from about 1:1.5 to about 1.5:1.

25 The components of the nonionic surfactant systems of the present invention are set forth below.

Polyhydroxy Fatty Acid Amide

30 The polyhydroxy fatty acid amide surfactant component of the present invention comprises compounds of the structural formula:



35 wherein: R^1 is H, C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C_1 - C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5 - C_{31} hydrocarbyl, preferably straight chain C_7 - C_{19} alkyl or alkenyl, more preferably straight chain C_9 - C_{17} alkyl or alkenyl, most preferably straight chain C_{11} - C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl

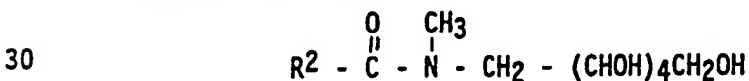
having a linear hydrocarbonyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxyated or propoxyated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$, $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxyated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$.

In Formula (I), R^1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

$\text{R}^2-\text{CO}-\text{N}<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

The most preferred polyhydroxy fatty acid amide has the general formula



wherein R^2 is a C_{11} - C_{17} straight-chain alkyl or alkenyl group.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making

compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and
5 U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

In one process for producing N-alkyl or N-hydroxyalkyl, N-deoxyglycyl fatty acid amides wherein the glycyl component
10 is derived from glucose and the N-alkyl or N-hydroxyalkyl functionality is N-methyl, N-ethyl, N-propyl, N-butyl, N-hydroxyethyl, or N-hydroxypropyl, the product is made by reacting N-alkyl- or N-hydroxyalkyl-glucamine with a fatty ester selected from fatty methyl esters, fatty ethyl esters, and fatty
15 triglycerides in the presence of a catalyst selected from the group consisting of trilithium phosphate, trisodium phosphate, tripotassium phosphate, tetrasodium pyrophosphate, pentapotassium tripolyphosphate, lithium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, disodium tartrate, dipotassium tartrate,
20 sodium potassium tartrate, trisodium citrate, tripotassium citrate, sodium basic silicates, potassium basic silicates, sodium basic aluminosilicates, and potassium basic aluminosilicates, and mixtures thereof. The amount of catalyst is preferably from about
25 0.5 mole % to about 50 mole %, more preferably from about 2.0 mole % to about 10 mole %, on an N-alkyl or N-hydroxyalkyl-glucamine molar basis. The reaction is preferably carried out at from about 138°C to about 170°C for typically from about 20 to about 90 minutes. When triglycerides are utilized in the reaction mixture
30 as the fatty ester source, the reaction is also preferably carried out using from about 1 to about 10 weight % of a phase transfer agent, calculated on a weight percent basis of total reaction mixture, selected from saturated fatty alcohol polyethoxylates, alkylpolyglycosides, linear glycamide surfactant, and mixtures thereof.
35

Preferably, this process is carried out as follows:

- (a) preheating the fatty ester to about 138°C to about 170°C;

(b) adding the N-alkyl or N-hydroxyalkyl glucamine to the heated fatty acid ester and mixing to the extent needed to form a two-phase liquid/liquid mixture;

(c) mixing the catalyst into the reaction mixture; and

5 (d) stirring for the specified reaction time.

Also preferably, from about 2% to about 20% of preformed linear N-alkyl/N-hydroxyalkyl, N-linear glucosyl fatty acid amide product is added to the reaction mixture, by weight of the reactants, as the phase transfer agent if the fatty ester is a triglyceride. This seeds the reaction, thereby increasing reaction rate. A detailed experimental procedure is provided below in the Experimental.

15 The polyhydroxy "fatty acid" amide materials used herein also offer the advantages to the detergent formulator that they can be prepared wholly or primarily from natural, renewable, non-petrochemical feedstocks and are degradable. They also exhibit low toxicity to aquatic life.

It should be recognized that along with the polyhydroxy fatty acid amides of Formula (I), the processes used to produce them will also typically produce quantities of nonvolatile by-product such as esteramides and cyclic polyhydroxy fatty acid amide. The level of these by-products will vary depending upon the particular reactants and process conditions. Preferably, the polyhydroxy fatty acid amide incorporated into the detergent compositions hereof will be provided in a form such that the polyhydroxy fatty acid amide-containing composition added to the detergent contains less than about 10%, preferably less than about 4%, of cyclic polyhydroxy fatty acid amide. The preferred processes described above are advantageous in that they can yield rather low levels of by-products, including such cyclic amide by-product.

30 Nonionic Surfactants

The nonionic surfactant systems of the present invention comprise, in addition to the polyhydroxy fatty acid amide component, one or more of the nonionic surfactants described herein. The nonionic surfactants described herein will hereinafter be referred to as "additional nonionic surfactants." Nonionic compounds other than these additional nonionic surfactants may be optionally included in the nonionic surfactant

systems of the present invention. These other, optional nonionic compounds will hereinafter be referred to as "optional nonionics." Without intending to be limited thereby, it is believed that when such optional nonionics are included in the nonionic surfactant systems of the present invention, they do not provide the unexpected stain-removal benefits already described herein.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the additional nonionic surfactant of the nonionic surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the additional nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow

- 11 -

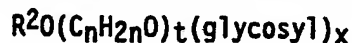
molecular weight distribution), both marketed by Union Carbide Corporation; Neodo1™ 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), Neodo1™ 23-6.5 (the condensation product of C₁₂-C₁₃ linear alcohol with 6.5 moles of ethylene oxide), Neodo1™ 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), Neodo1™ 45-4 (the condensation product of C₁₄-C₁₅ linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro™ EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company.

Also useful as the additional nonionic surfactant of the nonionic surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

Optionally, and less desirably, there can be a polyalkylene-oxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl

polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-
sides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-
sides and tallow alkyl tetra-, penta-, and hexagluco-
sides.

The preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

Although not preferred, the condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant of the nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available PluronicTM surfactants, marketed by BASF.

Also not preferred, although suitable for use as the additional nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Preferred for use as the additional nonionic surfactant of the nonionic surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

DETERGENT COMPOSITIONS

The present invention further provides laundry detergent compositions comprising at least 1% by weight, preferably from about 3% to about 65%, more preferably from about 10% to about 25% by weight of total surfactants. The surfactants of such laundry detergent compositions can comprise only the nonionic surfactant system of the present invention, or it may comprise the nonionic surfactant system in combination with other deterative surfactants, such as anionic, cationic, ampholytic, zwitterionic and semi-polar surfactants. The cationic surfactants useful herein are those having one long-chain hydrocarbly group.

The laundry detergent compositions of the present invention can also contain the optional nonionics already referred to herein, although it is believed that such optional nonionics do not provide the unexpected stain-removal benefits of the nonionic

surfactant systems of the present invention. When the laundry detergent compositions of the present invention contain the nonionic surfactant systems and such other, optional deterative surfactants, the weight ratio of the nonionic surfactant system to the other deterative surfactants will be in the range of from about 50:1 to about 1:10, preferably from about 10:1 to about 1:5. Additionally, the laundry detergent compositions of the present invention can optionally contain other ingredients typically found in detergent compositions, such as builders, soil release agents, chelating agents, etc.

When included in such laundry detergent compositions, the nonionic surfactant systems of the present invention act to improve the greasy/oily stain removal properties of such laundry detergent compositions across a broad range of laundry conditions.

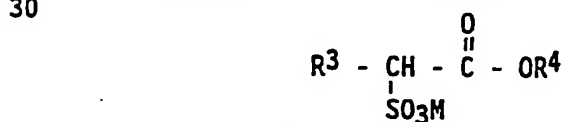
Anionic Surfactants

The laundry detergent compositions of the present invention can contain, in addition to the nonionic surfactant system of the present invention, one or more anionic surfactants as described below.

Alkyl Ester Sulfonate Surfactant

Alkyl ester sulfonate surfactants hereof include linear esters of C₈-C₂₀ carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO₃ according to "The Journal of the American Oil Chemists Society," 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:



wherein R³ is a C₈-C₂₀ hydrocarbyl, preferably an alkyl, or combination thereof, R⁴ is a C₁-C₆ hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such

- 15 -

as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10} - C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10} - C_{16} alkyl.

5 Alkyl Sulfate Surfactant

Alkyl sulfate surfactants hereof are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10} - C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10} - C_{20} alkyl component, more preferably a C_{12} - C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C_{12} -16 are preferred for lower wash temperatures (e.g., below about 50°C) and C_{16} -18 alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

20 Alkyl Alkoxylated Sulfate Surfactant

Alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10} - C_{24} alkyl or hydroxyalkyl group having a C_{10} - C_{24} alkyl component, preferably a C_{12} - C_{20} alkyl or hydroxyalkyl, more preferably C_{12} - C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12} - C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12} - $C_{18}E(1.0)M$), C_{12} - C_{18} alkyl polyethoxylate (2.25)

- 16 -

sulfate (C₁₂-C₁₈E(2.25)M), C₁₂-C₁₈ alkyl polyethoxylate (3.0) sulfate (C₁₂-C₁₈E(3.0)M), and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulfate (C₁₂-C₁₈E(4.0)M), wherein M is conveniently selected from sodium and potassium.

5 Other Anionic Surfactants

Other anionic surfactants useful for deterative purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C₉-C₂₀ linear alkylbenzenesulfonates, C₈-C₂₂ primary or secondary alkanesulfonates, C₈-C₂₄ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycoether-sulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfo-succinates, monoesters of sulfosuccinates (especially saturated and unsaturated C₁₂-C₁₈ monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C₆-C₁₂ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_k-CH₂COO⁻M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

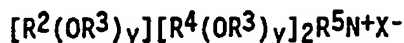
- 17 -

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

5 Other Surfactants

The laundry detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as nonionic surfactants other than those already described herein. However, without intending to be limited thereby, it is believed that nonionic surfactants other than those already described herein, including the semi-polar nonionic amine oxides described below, will not provide the hereinbefore discussed stain removal benefits associated with the nonionic surfactant system of the present invention.

15 Cationic deterative surfactants suitable for use in the laundry detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyl-dimethylammonium halogenides, and those surfactants having the formula:



wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1 - C_4 alkyl, C_1 - C_4 hydroxy-alkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

35 Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

- 18 -

When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 25%, preferably from about 3% to about 15% by weight of such cationic surfactants.

5 Ampholytic surfactants are also suitable for use in the laundry detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of
10 heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued
15 December 30, 1975 at column 19, lines 18-35 (herein incorporated by reference) for examples of ampholytic surfactants.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic
20 surfactants.

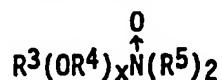
Zwitterionic surfactants are also suitable for use in laundry detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or
25 derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48 (herein incorporated by reference) for examples of zwitterionic surfactants.

30 When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

35 Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3

carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxy-alkyl groups containing from about 1 to about 3 carbon atoms; and
 5 water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine
 10 oxide surfactants having the formula



wherein R³ is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms;
 15 R⁴ is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R⁵ is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R⁵
 20 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides.

25 When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

Builders

30 The laundry detergent compositions of the present invention can comprise inorganic or organic detergent builders to assist in mineral hardness control.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. Liquid
 35 formulations typically comprise at least about 1%, more typically from about 5% to about 50%, preferably about 5% to about 30%, by weight of detergent builder. Granular formulations typically comprise at least about 1%, more typically from about 10% to about

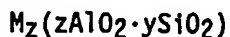
80%, preferably from about 15% to about 50% by weight of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

5 Inorganic detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesqui-
10 carbonates), sulfates, and aluminosilicates. Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions (hereinafter collectively "borate builders"), can also be used. Preferably, non-borate builders are used in compositions of the invention intended for use at wash conditions less than about
15 50°C, especially less than about 40°C.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates
20 described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck, incorporated herein by reference. However, other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

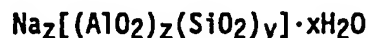
25 Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesquicarbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973, the disclosure of which is incorporated
30 herein by reference.

Aluminosilicate builders are especially useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid
35 detergent formulations. Aluminosilicate builders include those having the empirical formula:



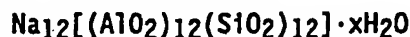
wherein M is sodium, potassium, ammonium or substituted ammonium,

z is from about 0.5 to about 2; and y is 1; this material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO_3 hardness per gram of anhydrous aluminosilicate. Preferred aluminosilicates are zeolite builders which have the formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al., issued October 12, 1976, incorporated herein by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Specific examples of polyphosphates are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta phosphate in which the degree of polymerization ranges from about 6 to about 21, and salts of phytic acid.

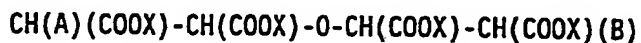
Examples of phosphonate builder salts are the water-soluble salts of ethane 1-hydroxy-1,1-diphosphonate particularly the sodium and potassium salts, the water-soluble salts of methylene diphosphonic acid e.g. the trisodium and tripotassium salts and the water-soluble salts of substituted methylene diphosphonic acids, such as the trisodium and tripotassium ethylidene, isopropylidene benzylmethylidene and halo methylidene phosphonates.

Phosphonate builder salts of the aforementioned types are disclosed in U.S. Patent Nos. 3,159,581 and 3,213,030 issued December 1, 1964 and October 19, 1965, to Diehl; U.S. Patent No. 3,422,021 issued January 14, 1969, to Roy; and U.S. Patent Nos. 3,400,148 and 3,422,137 issued September 3, 1968, and January 14, 1969 to

Quimby, said disclosures being incorporated herein by reference. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium salts, especially sodium salts, or ammonium and substituted ammonium (e.g., alkanolammonium) salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates. A number of ether polycarboxylates have been disclosed for use as detergent builders. Examples of useful ether polycarboxylates include oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al., U.S. Patent 3,635,830, issued January 18, 1972, both of which are incorporated herein by reference.

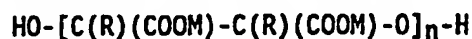
A specific type of ether polycarboxylates useful as builders in the present invention also include those having the general formula:



wherein A is H or OH; B is H or $-\text{O}-\text{CH(COOX)}-\text{CH}_2(\text{COOX})$; and X is H or a salt-forming cation. For example, if in the above general formula A and B are both H, then the compound is oxydisuccinic acid and its water-soluble salts. If A is OH and B is H, then the compound is tartrate monosuccinic acid (TMS) and its water-soluble salts. If A is H and B is $-\text{O}-\text{CH(COOX)}-\text{CH}_2(\text{COOX})$, then the compound is tartrate disuccinic acid (TDS) and its water-soluble salts. Mixtures of these builders are especially preferred for use herein. Particularly preferred are mixtures of TMS and TDS in a weight ratio of TMS to TDS of from about 97:3 to about 20:80. These builders are disclosed in U.S. Patent 4,663,071, issued to Bush et al., on May 5, 1987.

Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903, all of which are incorporated herein by reference.

5 Other useful detergency builders include the ether hydroxy-polycarboxylates represented by the structure:



wherein M is hydrogen or a cation wherein the resultant salt is water-soluble, preferably an alkali metal, ammonium or substituted ammonium cation, n is from about 2 to about 15 (preferably n is from about 2 to about 10, more preferably n averages from about 2 to about 4) and each R is the same or different and selected from hydrogen, C₁₋₄ alkyl or C₁₋₄ substituted alkyl (preferably R is hydrogen).

15 Still other ether polycarboxylates include copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulfonic acid, and carboxymethyloxysuccinic acid.

20 Organic polycarboxylate builders also include the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids. Examples of polyacetic acid builder salts are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid and nitrilotriacetic acid.

25 Also included are polycarboxylates such as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, benzene pentacarboxylic acid, and carboxymethyloxysuccinic acid, and soluble salts thereof.

30 Citric builders, e.g., citric acid and soluble salts thereof, is a polycarboxylate builder of particular importance for heavy duty liquid detergent formulations, but can also be used in granular compositions. Suitable salts include the metal salts such as sodium, lithium, and potassium salts, as well as ammonium and substituted ammonium salts.

35 Other carboxylate builders include the carboxylated carbohydrates disclosed in U.S. Patent 3,723,322, Diehl, issued March 28, 1973, incorporated herein by reference.

Also suitable in the laundry detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986, incorporated herein by reference. Useful succinic acid builders include the C₅-C₂₀ alkyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Alkyl succinic acids typically are of the general formula $R-CH(COOH)CH_2(COOH)$ i.e., derivatives of succinic acid, wherein R is hydrocarbon, e.g., C₁₀-C₂₀ alkyl or alkenyl, preferably C₁₂-C₁₆ or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents, all as described in the above-mentioned patents.

The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts.

Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Examples of useful builders also include sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentane-tetracarboxylate, water-soluble polyacrylates (these polyacrylates having molecular weights to above about 2,000 can also be effectively utilized as dispersants), and the copolymers of maleic anhydride with vinyl methyl ether or ethylene.

Other suitable polycarboxylates are the polyacetal carboxylates disclosed in U.S. Patent 4,144,226, Crutchfield et al., issued March 13, 1979, incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together, under polymerization conditions, an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

- 25 -

Polycarboxylate builders are also disclosed in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

Other organic builders known in the art can also be used. For example, monocarboxylic acids, and soluble salts thereof, having long chain hydrocarbyls can be utilized. These would include materials generally referred to as "soaps." Chain lengths of C₁₀-C₂₀ are typically utilized. The hydrocarbyls can be saturated or unsaturated.

Enzymes

Deterative enzymes can be included in the laundry detergent compositions of the present invention for a variety of reasons including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and prevention of refugee dye transfer. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B.subtilis* and *B.licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name Esperase®. The preparation of this enzyme and analogous enzymes is described in British patent specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE™ and SAVINASE™ by Novo Industries A/S (Denmark) and MAXATASE™ by International Bio-Synthetics, Inc. (The Netherlands).

Of interest in the category of proteolytic enzymes, especially for liquid detergent compositions, are enzymes referred to herein as Protease A and Protease B. Protease A and methods for its preparation are described in European Patent Application 130,756, published January 9, 1985, incorporated herein by reference. Protease B is a proteolytic enzyme which differs from Protease A in that it has a leucine substituted for tyrosine in position 217 in its amino acid sequence. Protease B is described in European Patent Application Serial No. 87303761.8, filed April 28, 1987, incorporated herein by reference. Methods for preparation of Protease B are also disclosed in European Patent Application 130,756, Bott et al., published January 9, 1985, incorporated herein by reference.

Amylases include, for example, α -amylases obtained from a special strain of *B.licheniformis*, described in more detail in British patent specification No. 1,296,839 (Novo), previously incorporated herein by reference. Amylolytic proteins include, for example, RAPIDASETM, International Bio-Synthetics, Inc. and TERMAMYLTM, Novo Industries.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al., issued March 6, 1984, incorporated herein by reference, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800, and cellulases produced by a fungus of *Bacillus* N or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusc (*Dolabella Auricula* Solander).

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent No. 1,372,034, incorporated herein by reference. Suitable lipases include those which show a positive immunological cross-reaction

- 27 -

with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase and a method for its purification have been described in Japanese Patent Application No. 53-20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Such lipases of the present invention should show a positive immunological cross reaction with the Amano-P antibody, using the standard and well-known immunodiffusion procedure according to Ouchterlony (Acta. Med. Scan., 133, pages 76-79 (1950)). These lipases, and a method for their immunological cross-reaction with Amano-P, are also described in U.S. Patent 4,707,291, Thom et al., issued November 17, 1987, incorporated herein by reference. Typical examples thereof are the Amano-P lipase, the lipase ex *Pseudomonas fragi* FERM P 1339 (available under the trade name Amano-B), lipase ex *Pseudomonas nitroreducens* var. *lipolyticum* FERM P 1338 (available under the trade name Amano-CES), lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S, incorporated herein by reference.

A wide range of enzyme materials and means for their incorporation into synthetic detergent granules is also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. (incorporated herein by reference). Enzymes are further disclosed

in U.S. Patent No. 4,101,457, Place et al., issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both incorporated herein by reference. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al., issued April 14, 1981, also incorporated herein by reference.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.05 mg to about 3 mg, of active enzyme per gram of the composition.

For granular detergents, the enzymes are preferably coated or prilled with additives inert toward the enzymes to minimize dust formation and improve storage stability. Techniques for accomplishing this are well known in the art. In liquid formulations, an enzyme stabilization system is preferably utilized. Enzyme stabilization techniques for aqueous detergent compositions are well known in the art. For example, one technique for enzyme stabilization in aqueous solutions involves the use of free calcium ions from sources such as calcium acetate, calcium formate, and calcium propionate. Calcium ions can be used in combination with short chain carboxylic acid salts, preferably formates. See, for example, U.S. Patent 4,318,818, Letton, et al., issued March 9, 1982, incorporated herein by reference. It has also been proposed to use polyols like glycerol and sorbitol. Alkoxy-alcohols, dialkylglycoethers, mixtures of polyvalent alcohols with polyfunctional aliphatic amines (e.g., alkanolamines such as diethanolamine, triethanolamine, di-isopropanolamine, etc.), and boric acid or alkali metal borate. Enzyme stabilization techniques are additionally disclosed and exemplified in U.S. Patent 4,261,868, issued April 14, 1981 to Horn, et al., U. S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al., both incorporated herein by reference, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Non-boric acid and borate stabilizers are preferred. Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319, and 3,519,570.

Bleaching Compounds - Bleaching Agents and Bleach Activators

The laundry detergent compositions of the present invention may contain bleaching agents or bleaching compositions containing

bleaching agent and one or more bleach activators. When included, present bleaching compounds will typically comprise from about 1% to about 20%, more typically from about 1% to about 10%, of such laundry detergent composition. In general, bleaching compounds
5 are optional components in non-liquid formulations, e.g., granular detergents. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition.

The bleaching agents used herein can be any of the bleaching
10 agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. For wash conditions below about 50°C, especially below about 40°C, it is preferred that the compositions
15 hereof not contain borate or material which can form borate in situ (i.e. borate-forming material) under detergent storage or wash conditions. Thus it is preferred under these conditions that a non-borate, non-borate-forming bleaching agent is used. Preferably, detergents to be used at these temperatures are substantially free of borate and borate-forming material. As used
20 herein, "substantially free of borate and borate-forming material" shall mean that the composition contains not more than about 2% by weight of borate-containing and borate-forming material of any type, preferably, no more than 1%, more preferably 0%.

One category of bleaching agent that can be used encompasses
25 percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloroperbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and
30 diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al., filed June 3, 1985, European Patent Application 0,133,354, Banks et al., published February 20, 1985, and U.S. Patent 4,412,934, Chung et al., issued
35 November 1, 1983, all of which are incorporated by reference herein. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent

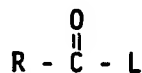
4,634,551, issued January 6, 1987 to Burns, et al., incorporated herein by reference.

5 Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulfonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

10 Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide.

15 Peroxygen bleaching agents are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator.

20 Preferred bleach activators incorporated into the laundry detergent compositions of the present invention have the general formula:



25 wherein R is an alkyl group containing from about 1 to about 18 carbon atoms wherein the longest linear alkyl chain extending from and including the carbonyl carbon contains from about 6 to about 10 carbon atoms and L is a leaving group, the conjugate acid of which has a pK_a in the range of from about 4 to about 13. These bleach activators are described in U.S. Patent 4,915,854, issued April 10, 1990 to Mao, et al., incorporated herein by reference, and U.S. Patent 4,412,934, which was previously incorporated herein by reference.

35 Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photo-activated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out

- 31 -

to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718, issued July 5, 1977 to
5 Holcombe et al., incorporated herein by reference. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

Polymeric Soil Release Agent

Any polymeric soil release agents known to those skilled in
10 the art can be employed in the laundry detergent compositions of the present invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and
15 remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

20 Polymeric soil release agents include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like.

25 Cellulosic derivatives that are functional as soil release agents are commercially available and include hydroxyethers of cellulose such as Methocel[®] (Dow).

Cellulosic soil release agents also include those selected from the group consisting of C₁-C₄ alkyl and C₄ hydroxyalkyl
30 cellulose such as methylcellulose, ethylcellulose, hydroxypropyl methylcellulose, and hydroxybutyl methylcellulose. A variety of cellulose derivatives useful as soil release polymers are disclosed in U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al., incorporated herein by reference.

35 Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide

backbones. Such materials are known in the art and are described in European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Suitable commercially available soil release agents of this kind include the SokalanTM type of material, e.g., SokalanTM HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. More specifically, these polymers are comprised of repeating units of ethylene terephthalate and PEO terephthalate in a mole ratio of ethylene terephthalate units to PEO terephthalate units of from about 25:75 to about 35:65, said PEO terephthalate units containing polyethylene oxide having molecular weights of from about 300 to about 2000. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976, which is incorporated by reference. See also U.S. Patent 3,893,929 to Basadur issued July 8, 1975 (incorporated by reference) which discloses similar copolymers.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units containing 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000, and the mole ratio of ethylene terephthalate units to polyoxyethylene terephthalate units in the polymeric compound is between 2:1 and 6:1. Examples of this polymer include the commercially available material Zelcon^R 5126 (from Dupont) and Milease^R T (from ICI). These polymers and methods of their preparation are more fully described in U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink, which is incorporated herein by reference.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone, said soil release agent being derived from allyl alcohol ethoxylate, dimethylterephthalate, and 1,2 propylene diol, wherein the terminal moieties of each oligomer

have, on average, a total of from about 1 to about 4 sulfonate groups. These soil release agents are described fully in U.S. Patent 4,968,451, issued November 6, 1990 to J. J. Scheibel and E. P. Gosselink, U.S. Serial No. 07/474,709, filed January 29, 1990, incorporated herein by reference.

Other suitable polymeric soil release agents include the ethyl- or methyl-capped 1,2-propylene terephthalate-polyoxyethylene terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al., the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, wherein the anionic end-caps comprise sulfo-polyethoxy groups derived from polyethylene glycol (PEG), the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink, having polyethoxy end-caps of the formula $X-(OCH_2CH_2)_n$ wherein n is from 12 to about 43 and X is a C_1 - C_4 alkyl, or preferably methyl, all of these patents being incorporated herein by reference.

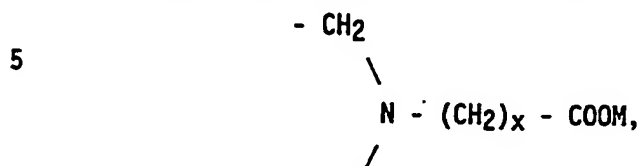
Additional soil release polymers include the soil release polymers of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al., which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters, said patent being incorporated herein by reference. The terephthalate esters contain unsymmetrically substituted oxy-1,2-alkyleneoxy units.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, preferably from about 0.1% to about 5.0%, more preferably from about 0.2% to about 3.0% by weight of the laundry detergent compositions of the present invention.

Chelating Agents

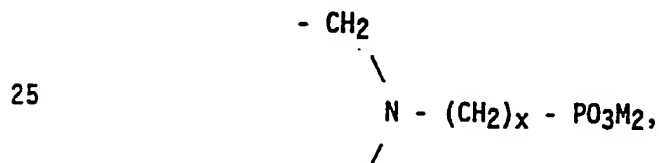
The laundry detergent compositions of the present invention may also optionally contain one or more iron and manganese chelating agents as a builder adjunct material. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents in compositions of the invention can have one or more, preferably at least two, units of the substructure



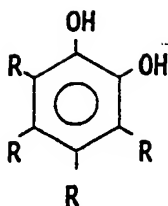
wherein M is hydrogen, alkali metal, ammonium or substituted ammonium (e.g. ethanolamine) and x is from 1 to about 3, preferably 1. Preferably, these amino carboxylates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms. Operable amine carboxylates include ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-
10 acetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts thereof and mixtures thereof.

Amino phosphonates are also suitable for use as chelating agents in the laundry detergent compositions of the present invention when at least low levels of total phosphorus are permitted in detergent compositions. Compounds with one or more, preferably at least two, units of the substructure



wherein M is hydrogen, alkali metal, ammonium or substituted ammonium and x is from 1 to about 3, preferably 1, are useful and include ethylenediaminetetrakis (methylenephosphonates), nitrilo-
30 tris (methylenephosphonates) and diethylenetriaminepentakis (methylenephosphonates). Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms. Alkylene groups can be shared by substructures.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. These materials can comprise compounds having the general formula



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wherein at least one R is $-SO_3H$ or $-COOH$ or soluble salts thereof and mixtures thereof. U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al., incorporated herein by reference, discloses polyfunctionally - substituted aromatic chelating and sequestering agents. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene. Alkaline detergent compositions can contain these materials in the form of alkali metal, ammonium or substituted ammonium (e.g. mono-or triethanol-amine) salts.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the laundry detergent compositions of the present invention. More preferably chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

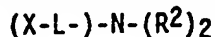
Clay Soil Removal/Anti-redeposition Agents

Clay soil removal/anti-redeposition agents useful in the laundry detergent compositions of the present invention include polyethylene glycols and water-soluble ethoxylated amines having clay soil removal and anti-redeposition properties.

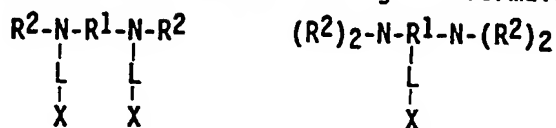
Polyethylene glycol compounds useful in the laundry detergent compositions of the present invention typically have a molecular weight in the range of from about 400 to about 100,000, preferably from about 1,000 to about 20,000, more preferably from about 2,000 to about 12,000, most preferably from about 4,000 to about 8,000. Such compounds are commercially available and are sold as Carbowax®, which is available from Union Carbide, located in Danbury, Conn.

The water-soluble ethoxylated amines are preferably selected from the group consisting of:

(1) ethoxylated monoamines having the formula:



(2) ethoxylated diamines having the formula:

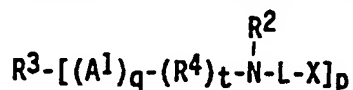


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or

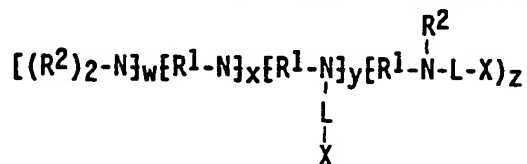


(3) ethoxylated polyamines having the formula:



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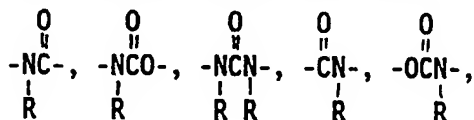
(4) ethoxylated amine polymers having the general formula:



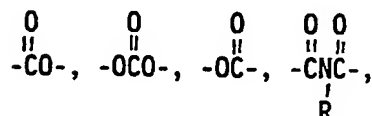
15

and

(5) mixtures thereof; wherein A¹ is



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or -O-; R is H or C₁-C₄ alkyl or hydroxyalkyl; R¹ is C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R² is C₁-C₄ or hydroxyalkyl, the moiety -L-X, or two R² together form the moiety -(CH₂)_r, -A²-(CH₂)_s-, wherein A² is -O- or -CH₂-, r is 1 or 2, s is 1 or 2, and r + s is 3 or 4; X is a nonionic group, an anionic group or mixture thereof; R³ is a substituted C₃-C₁₂ alkyl, hydroxyalkyl, alkenyl, aryl, or alkaryl group having substitution sites; R⁴ is C₁-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed; L is a hydrophilic chain which contains the polyoxyalkylene moiety -[(R⁵)_m(CH₂CH₂O)_n]-, wherein R⁵ is C₃-C₄ alkylene or hydroxyalkylene and m and n are numbers such that the moiety

- 37 -

5 $-(CH_2CH_2O)_n-$ comprises at least about 50% by weight of said polyoxyalkylene moiety; for said monoamines, m is from 0 to about 4, and n is at least about 12; for said diamines, m is from 0 to about 3, and n is at least about 6 when R^1 is C₂-C₃ alkylene, hydroxyalkylene, or alkenylene, and at least about 3 when R^1 is other than C₂-C₃ alkylene, hydroxyalkylene or alkenylene; for said polyamines and amine polymers, m is from 0 to about 10 and n is at least about 3; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1; w is 1 or 0; x + y + z is at least 2; and y + z is at least 2. The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986, incorporated herein by reference. Another group of preferred clay soil removal/anti-redeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984, incorporated herein by reference. Other clay soil removal/anti-redeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985, all of which are incorporated herein by reference.

25 The most preferred soil release and anti-redeposition agents are ethoxylated tetraethylenepentamine and the polyethylene glycols having a molecular weight in the range of from about 4,000 to about 8,000.

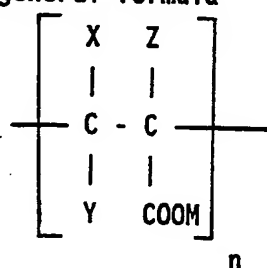
30 Granular detergent compositions which contain such compounds typically contain from about 0.01% to about 10.0% by weight of the clay removal agent; liquid detergent compositions typically contain from about 0.01% to about 5.0% by weight.

Polymeric Dispersing Agents

35 Polymeric polycarboxylate dispersing agents can advantageously be utilized in the laundry detergent compositions of the present invention. These materials can aid in calcium and magnesium hardness control. In addition to acting as a builder adjunct analogously to the polycarboxylate described above in the Builder

description, it is believed, though it is not intended to be limited by theory, that these higher molecular weight dispersing agents can further enhance overall detergent builder performance by inhibiting crystal growth of inorganics, by particulate soil peptization, and by antiredepositions, when used in combination with other builders including lower molecular weight polycarboxylates.

The polycarboxylate materials which can be employed as the polymeric polycarboxylate dispersing agent are these polymers or copolymers which contain at least about 60% by weight of segments with the general formula



wherein X, Y, and Z are each selected from the group consisting of hydrogen, methyl, carboxy, carboxymethyl, hydroxy and hydroxymethyl; a salt-forming cation and n is from about 30 to about 400. Preferably, X is hydrogen or hydroxy, Y is hydrogen or carboxy, Z is hydrogen and M is hydrogen, alkali metal, ammonia or substituted ammonium.

Polymeric polycarboxylate materials of this type can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in

- 39 -

the acid form ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent No. 3,308,067, issued March 7, 1967. This patent is incorporated herein by reference.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form ranges from about 5,000 to 100,000, preferably from about 6,000 to 60,000, more preferably from about 7,000 to 60,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, which publication is incorporated herein by reference.

If utilized, the polymeric dispersing agents will generally comprise from about 0.2% to about 10%, preferably from about 1% to about 5% by weight of the laundry detergent compositions.

Brightener

Optical brighteners or other brightening or whitening agents known to those skilled in the art can be incorporated into the laundry detergent compositions of the present invention. However, the choice of brightener will depend upon a number of factors, such as the type of detergent, the nature of other components present in the detergent composition, the temperatures of wash water, the degree of agitation, and the ratio of the material washed to tub size.

The brightener selection is also dependent upon the type of material to be cleaned, e.g., cottons, synthetics, etc. Since most laundry detergent products are used to clean a variety of

fabrics, the detergent compositions should contain a mixture of brighteners which will be effective for a variety of fabrics. It is of course necessary that the individual components of such a brightener mixture be compatible.

5 Commercial optical brighteners can be classified into subgroups which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphen-5,5-dioxide, azoles, 5- and 10 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982), the disclosure of which is incorporated herein by reference.

15 Stilbene derivatives include, but are not necessarily limited to, derivatives of bis(triazinyl)amino-stilbene; bisacylamino derivatives of stilbene; triazole derivatives of stilbene; oxadiazole derivatives of stilbene; oxazole derivatives of stilbene; and styryl derivatives of stilbene.

20 Certain derivatives of bis(triazinyl)aminostilbene may be prepared from 4,4'-diamine-stilbene-2,2'-disulfonic acid.

Coumarin derivatives include, but are not necessarily limited to, derivatives substituted in the 3-position, in the 7-position, and in the 3- and 7-positions.

25 Carboxylic acid derivatives include, but are not necessarily limited to, fumaric acid derivatives; benzoic acid derivatives; p-phenylene-bis-acrylic acid derivatives; naphthalenedicarboxylic acid derivatives; heterocyclic acid derivatives; and cinnamic acid derivatives.

30 Cinnamic acid derivatives can be further subclassified into groups which include, but are not necessarily limited to, cinnamic acid derivatives, styrylazoles, styrylbenzofurans, styryloxadiazoles, styryltriazoles, and styrylpolyphenyls, as disclosed on page 77 of the Zahradnik reference.

35 The styrylazoles can be further subclassified into styrylbenzoxazoles, styrylimidazoles and styrylthiazoles, as disclosed on page 78 of the Zahradnik reference. It will be understood that these three identified subclasses may not necessarily reflect an

- 41 -

exhaustive list of subgroups into which styrylazoles may be subclassified.

5 Other optical brighteners are the derivatives of dibenzothio-
phene-5,5-dioxide disclosed at page 741-749 of The Kirk-Othmer
Encyclopedia of Chemical Technology, Volume 3, pages 737-750 (John
Wiley & Son, Inc., 1962), the disclosure of which is incorporated
herein by reference, and include 3,7-diaminodibenzothiophene-2,8-
disulfonic acid 5,5 dioxide.

10 Other optical brighteners are azoles, which are derivatives
of 5-membered ring heterocycles. These can be further subcategor-
ized into monoazoles and bisazoles. Examples of monoazoles and
bisazoles are disclosed in the Kirk-Othmer reference.

15 Still other optical brighteners are the derivatives of
6-membered-ring heterocycles disclosed in the Kirk-Othmer refer-
ence. Examples of such compounds include brighteners derived from
pyrazine and brighteners derived from 4-aminonaphthalamide.

20 In addition to the brighteners already described, miscellane-
ous agents may also be useful as brighteners. Examples of such
miscellaneous agents are disclosed at pages 93-95 of the Zahradnik
reference, and include 1-hydroxy-3,6,8-pyrenetri- sulfonic acid;
2,4-dimethoxy-1,3,5-triazin-6-yl-pyrene; 4,5-di- phenylimidazol-
onedisulfonic acid; and derivatives of pyrazoline- quinoline.

25 Other specific examples of optical brighteners are those
identified in U.S. Patent 4,790,856, issued to Wixon on December
13, 1988, the disclosure of which is incorporated herein by
reference. These brighteners include the PhorwhiteTM series of
brighteners from Verona. Other brighteners disclosed in this
reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM;
30 available from Ciba-Geigy; Arctic White CC and Artic White CWD,
available from Hilton-Davis, located in Italy; the 2-(4-styryl-
phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-
yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the γ -amino-
coumarins. Specific examples of these brighteners include
4-methyl-7-diethylamino coumarin; 1,2-bis(-benzimidazol-2-yl)-
35 ethylene; 1,3-diphenylphrazolines; 2,5-bis(benzoxazol-2-yl)-
thiophene; 2-styryl-naphth-[1,2-d]-oxazole; and 2-(stilbene-4-yl)-
2H-naphtho[1,2-d]triazole.

Still other optical brighteners include those disclosed in U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton, the disclosure of which is incorporated herein by reference.

5 If utilized, the optical brighteners will generally comprise from about 0.05% to about 2.0%, preferably from about 0.1% to about 1.0% by weight of the laundry detergent compositions.

Suds Suppressors

10 Compounds known, or which become known, for reducing or suppressing the formation of suds can be incorporated into the laundry detergent compositions of the present invention. The incorporation of such materials, hereinafter "suds suppressors," can be desirable because the polyhydroxy fatty acid amide surfactants hereof can increase suds stability of the detergent compositions. Suds suppression can be of particular importance 15 when the detergent compositions include a relatively high sudsing surfactant in combination with the polyhydroxy fatty acid amide surfactant. Suds suppression is particularly desirable for compositions intended for use in front loading automatic washing machines. These machines are typically characterized by having 20 drums, for containing the laundry and wash water, which have a horizontal axis and rotary action about the axis. This type of agitation can result in high suds formation and, consequently, in reduced cleaning performance. The use of suds suppressors can also be of particular importance under hot water washing 25 conditions and under high surfactant concentration conditions.

A wide variety of materials may be used as suds suppressors. Suds suppressors are well known to those skilled in the art. They are generally described, for example, in Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 30 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acids and soluble salts thereof. These materials are discussed in U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John, said patent being incorporated herein by reference. The monocar- 35 boxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts,

and ammonium and alkanolammonium salts. These materials are a preferred category of suds suppressor for detergent compositions.

5 The laundry detergent compositions of the present invention may also contain non-surfactant suds suppressors. These include, for example, high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid
10 esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chlor-
15 ide with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and mono-
stearyl di-alkali metal (e.g., sodium, potassium, lithium) phos-
20 phates and phosphate esters. The hydrocarbons, such as paraffin and haloparaffin, can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 5°C, and a minimum boiling point not less than about
25 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5,
30 1981 to Gandolfo, et al., incorporated herein by reference. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mix-
tures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds comprises
35 silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to

Gandolfo et al. and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S., both incorporated herein by reference.

5 Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

10 Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al., and in U.S. Patent 4,652,392, Baginski et al., issued March 24, 1987.

15 An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1500 cs. at 25°C;
- 20 (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units of SiO_2 units in a ratio of from $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and to SiO_2 units of from about 0.6:1 to about 1.2:1; and
- (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel;

25 Suds suppressors, when utilized, are present in a "suds suppressing amount." By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will control the suds to the extent desired. The amount of suds control will vary with the detergent surfactant selected. For example, with high sudsing surfactants, relatively more of the suds controlling agent is used to achieve the desired suds control than with low foaming surfactants.

30 The laundry detergent compositions of the present invention will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts thereof, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is

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utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphates are generally utilized in amounts ranging from about 0.1% to about 2% by weight of the compositions.

Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used.

Other Ingredients

A wide variety of other ingredients which can be included in the laundry detergent compositions of the present invention include other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, etc.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from about 2 to about 6 carbon atoms and from about 2 to about 6 hydroxy groups (e.g., propylene glycol, ethylene glycol, glycerine, and 1,3-propanediol) can also be used.

The laundry detergent compositions of the present invention will preferably be formulated such that during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and about 10.5. Liquid product formulations preferably have a pH between about 7.5 and about 9.5, more preferably between about 7.5 and about 9.0. Techniques for controlling pH at recommended usage levels include the use of buffers, alkali, acids, etc., and are well known to those skilled in the art.

5 This invention further provides a method for cleaning substrates, such as fibers, fabrics, hard surfaces, skin, etc., by contacting said substrate with a detergent composition containing the nonionic surfactant system of the present invention, wherein
10 the weight ratio of polyhydroxy fatty acid amide to additional surfactant in the nonionic surfactant system is in the range of from about 1:5 to about 5:1, in the presence of a solvent such as water or a water-miscible solvent (e.g., primary and secondary alcohols). Agitation is preferably provided for enhancing
15 cleaning. Suitable means for providing agitation include rubbing by hand preferably with the aid of a brush, or other cleaning device, automatic laundry washing machines, automatic dishwashers, etc.

EXPERIMENTAL

15 This exemplifies a process for making a N-methyl, 1-deoxy-glucityl lauramide surfactant for use herein. Although a skilled chemist can vary apparatus configuration, one suitable apparatus for use herein comprises a three-liter four-necked flask fitted with a motor-driven paddle stirrer and a thermometer of length
20 sufficient to contact the reaction medium. The other two necks of the flask are fitted with a nitrogen sweep and a wide-bore side-arm (caution: a wide-bore side-arm is important in case of very rapid methanol evolution) to which is connected an efficient collecting condenser and vacuum outlet. The latter is connected
25 to a nitrogen bleed and vacuum gauge, then to an aspirator and a trap. A 500 watt heating mantle with a variable transformer temperature controller ("Variac") used to heat the reaction is so placed on a lab-jack that it may be readily raised or lowered to further control temperature of the reaction.

30 N-methylglucamine (195 g., 1.0 mole, Aldrich, M4700-0) and methyl laurate (Procter & Gamble CE 1270, 220.9 g., 1.0 mole) are placed in a flask. The solid/liquid mixture is heated with stirring under a nitrogen sweep to form a melt (approximately 25 minutes). When the melt temperature reaches 145° C, catalyst
35 (anhydrous powdered sodium carbonate, 10.5 g., 0.1 mole, J. T. Baker) is added. The nitrogen sweep is shut off and the aspirator and nitrogen bleed are adjusted to give 5 inches (5/31 atm.) Hg. vacuum. From this point on, the reaction temperature is held at

150° C by adjusting the Variac and/or by raising or lowering the mantle.

5 Within 7 minutes, first methanol bubbles are sighted at the meniscus of the reaction mixture. A vigorous reaction soon follows. Methanol is distilled over until its rate subsides. The vacuum is adjusted to give about 10 inches Hg. (10/31 atm.) vacuum. The vacuum is increased approximately as follows (in inches Hg. at minutes): 10 at 3, 20 at 7, 25 at 10. 11 minutes from the onset of methanol evolution, heating and stirring are discontinued co-incident with some foaming. The product is cooled and solidifies.

10 The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention, said scope being determined according to claims which follow.

EXAMPLES

The following examples of liquid detergent compositions are prepared according to the description set forth below:

20 A surfactant paste is initially formed by combining any desired surfactants with water and alcohol. The surfactants contained in this surfactant paste include the polyhydroxy fatty acid amides of the present invention. Ideally the surfactant paste should be pumpable at room or elevated temperatures.

25 Separately, non-aqueous solvents, the surfactant paste or solution, melted fatty acids, aqueous solutions of polycarboxylate builders and other salts, aqueous ethoxylated tetraethylenepent-amine, buffering agents, caustic, and water are combined in a mixing vessel. The pH is adjusted using either an aqueous citric acid solution or sodium hydroxide solution to a level of about 30 8.5. After the pH is adjusted, the final ingredients, such as soil release agents, enzymes, colorants and perfume, are added. The resulting mixture is stirred until a single phase compositions is obtained.

EXAMPLES 1-2

35 These examples are of heavy-duty liquid detergent compositions containing polyhydroxy fatty acid amide/additional nonionic surfactant systems.

- 48 -

		Example No. (wt. %)	
<u>Component</u>		<u>1</u>	<u>2</u>
5	C ₁₂₋₁₄ alkyl N-methyl glucamide	10.00	15.00
	C ₁₂₋₁₃ alkyl ethoxylate (6.5 ave.)	15.00	10.00
	Coco fatty acid	3.00	3.00
	Dodecyl trimethyl ammonium chloride	0.18	0.18
	Citric acid	1.00	1.00
10	Monoethanolamine	2.50	2.50
	Ethoxylated tetra-ethylenepentamine	1.50	1.50
	Protease (1 AU/gm)	0.53	0.53
15	Water & misc. (solvents, soil release polymers, perfumes, dyes, etc.)	--- balance to 100% ---	

EXAMPLES 3-7

20 These examples show heavy-duty liquid detergent compositions containing polyhydroxy fatty acid amide/additional nonionic surfactant systems in combination with anionic surfactants.

		Example No. (wt. %)				
<u>Component</u>		<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
25	C ₁₂₋₁₄ alkyl N-methyl glucamide	4.20	5.62	16.88	6.25	5.00
	C ₁₂₋₁₃ alkyl ethoxylate (6.5 ave.)	3.40	2.50	2.50	7.50	2.50
	C ₁₄₋₁₅ alkyl ethoxy (2.25 ave.) sulfate	12.60	16.88	5.62	-	7.50
30	Sodium C ₁₅₋₁₆ paraffin sulfonate	-	-	-	11.25	10.00
	Tartrate monosuccinate/ tartrate disuccinate	3.40	-	-	-	-
	Coco fatty acid	3.00	3.00	3.00	3.00	3.00
35	Dodecyl trimethyl ammonium chloride	0.51	0.18	0.18	0.18	0.18
	Citric acid	3.40	1.00	1.00	1.00	1.00

- 49 -

	Monoethanolamine	1.05	2.50	2.50	2.50	2.50
	Ethoxylated tetra- ethylenepentamine	1.50	1.50	1.50	1.50	1.50
	Brighteners	0.11	0.11	0.11	-	-
5	Protease (1 AU/gm)	0.80	0.51	0.51	0.53	0.53
	Amylase (325M AmU)	-	0.24	0.24	-	-
	Propanediol	4.50	4.00	4.00	-	-
	Ethanol	1.18	3.00	3.00	-	-
	NaOH (pH adjustment)	3.00	1.50	1.50	-	-
10	Calcium formate	0.29	0.89	0.89	-	-
	Sodium formate	0.34	0.34	0.34	-	-
	Sodium toluene sulfonate/ sodium cumene sulfonate	2.91	2.00	2.00	-	-
	Water & misc.	--- balance to 100% ---				
15	(solvents, soil release polymers, perfumes, dyes, etc.)					

EXAMPLES 8-10

20 These examples show highly built, heavy-duty liquid detergent compositions containing polyhydroxy fatty acid amide/additional nonionic surfactant systems in combination with anionic surfactants.

		Example No. (wt. %)		
<u>Component</u>		<u>8</u>	<u>9</u>	<u>10</u>
25	C ₁₂₋₁₄ alkyl N-methyl glucamide	3.10	3.10	4.10
	C ₁₂₋₁₃ alkyl ethoxylate (6.5 ave.)	9.30	3.10	2.10
30	C ₁₄₋₁₅ alkyl ethoxy (2.25 ave.) sulfate	-	3.00	4.00
	Sodium C ₁₅₋₁₆ paraffin sulfonate	-	3.10	-
	C _{11.8} linear alkyl benzene sulfonate	-	-	3.10
35	Tartrate monosuccinate/ tartrate disuccinate	-	10.00	-
	Citric acid	-	10.00	20.00
	Oxydisuccinate	20.00	-	-

- 50 -

	Polyacrylate (4500 mw)	1.50	1.50	1.50
	Monoethanolamine	1.00	1.00	1.00
	Brighteners	0.11	0.11	0.11
	Maxacal	0.21	0.21	0.21
5	Propanediol	5.50	5.50	5.50
	Ethanol	0.87	0.87	0.87
	NaOH (pH adjustment)	1.39	1.39	1.39
	Calcium formate	0.21	0.21	0.21
	Sodium formate	0.34	0.34	0.34
10	Sodium toluene sulfonate/ sodium cumene sulfonate	5.00	5.00	5.00
	Water & misc.	--- balance to 100% ---		
	(solvents, soil release polymers, perfumes, dyes, etc.)			

EXAMPLES 11-13

Examples of heavy-duty liquid detergent compositions containing an alkylpolysaccharide as the additional nonionic surfactant in the nonionic surfactant systems are as follows. These examples are intended for wash temperatures below about 50°C, and a preferred usage concentration of about 2,000 ppm, on a wash water weight basis, and are prepared in the same manner as the compositions of Examples 1-10.

	<u>Component</u>	<u>Example No. (Wt. %)</u>		
		<u>11</u>	<u>12</u>	<u>13</u>
25	C ₁₂₋₁₄ alkyl N-methyl glucamide	15.0	10.0	8.0
	C ₁₂₋₁₄ alkyl polyglyco- side (1.4 ave.)	10.0	10.0	-
30	C ₁₄₋₁₅ alkyl ethoxylate (7.0 ave.)	-	-	10.0
	C ₁₂₋₁₄ alkyl ethoxylate (7.0 ave.)	-	5.0	-
35	Dodecyl dimethyl amine oxide	-	-	4.0
	C ₁₂₋₁₄ fatty acid	3.0	3.0	-
	Dodecyl trimethyl ammonium chloride	0.2	0.2	-

- 51 -

	Ditallow dimethyl ammonium chloride	-	-	3.6
	Citric acid	1.0	1.0	-
	Monoethanolamine	2.5	2.5	-
5	Ethoxylated tetra-ethylenepentamine	1.5	1.5	1.5
	Optional ingredients and solvents	-- balance to 100% --		

EXAMPLES 14-15

10 The following examples of heavy-duty granular detergent compositions containing polyhydroxy fatty acid amide/additional nonionic surfactant systems. These compositions are intended for usage below about 50-60°C, and at a concentration of about 800 ppm, wash water weight basis. These compositions are prepared by

15 mixing a concentrated paste containing the amide, alkyl ethoxylate, brightener, and about 20 wt. % water, with any necessary dry ingredients in a high speed shear mixer, such as an Eirich RV02 mixer. Other dry optional ingredients in granular or powdered form can be admixed with the concentrated paste and necessary dry

20 ingredients in the high speed shear mixer, or may be subsequently added in a rotary mix drum.

		Example No. (Wt. %)	
<u>Component</u>		<u>14</u>	<u>15</u>
25	C ₁₂₋₁₄ alkyl N-methyl glucamide	8.0	10.0
	C ₁₂₋₁₅ alkyl ethoxylate (7.0 ave.)	12.0	10.0
	Zeolite A	30.0	15.0
	Sodium citrate	-	30.0
30	Sodium carbonate	30.0	20.0
	Brightener	1.0	1.0
	Optional ingredients	10.4	5.9
	Residual water	8.6	8.1
35		<u>100.0</u>	<u>100.0</u>

EXAMPLE 16

An alternate method for preparing the polyhydroxy fatty acid amides used herein is as follows. A reaction mixture consisting

- 52 -

of 84.87g. fatty acid methyl ester (source: Procter & Gamble methyl ester CE1270), 75g. N-methyl-D-glucamine (source: Aldrich Chemical Company M4700-0), 1.04g. sodium methoxide (source: Aldrich Chemical Company 16,499-2), and 68.51g. methyl alcohol is used. The reaction vessel comprises a standard reflux set-up fitted with a drying tube, condenser and stir bar. In this procedure, the N-methyl glucamine is combined with methanol with stirring under argon and heating is begun with good mixing (stir bar; reflux). After 15-20 minutes, when the solution has reached the desired temperature, the ester and sodium methoxide catalyst are added. Samples are taken periodically to monitor the course of the reaction, but it is noted that the solution is completely clear by 63.5 minutes. It is judged that the reaction is, in fact, nearly complete at that point. The reaction mixture is maintained at reflux for 4 hours. After removal of the methanol, the recovered crude product weighs 156.16 grams. After vacuum drying and purification, an overall yield of 106.92 grams purified product is recovered. However, percentage yields are not calculated on this basis, inasmuch as regular sampling throughout the course of the reaction makes an overall percentage yield value meaningless. The reaction can be carried out at 80% and 90% reactant concentrations for periods up to 6 hours to yield products with extremely small by-product formation.

The following is not intended to limit the invention herein, but is simply to further illustrate additional aspects of the technology which may be considered by the formulator in the manufacture of a wide variety of detergent compositions using the polyhydroxy fatty acid amides.

It will be readily appreciated that the polyhydroxy fatty acid amides are, by virtue of their amide bond, subject to some instability under highly basic or highly acidic conditions. While some decomposition can be tolerated, it is preferred that these materials not be subjected to pH's above about 11, preferably 10, nor below about 3 for unduly extended periods. Final product pH (liquids) is typically 7.0-9.0.

During the manufacture of the polyhydroxy fatty acid amides it will typically be necessary to at least partially neutralize

the base catalyst used to form the amide bond. While any acid can be used for this purpose, the detergent formulator will recognize that it is a simple and convenient matter to use an acid which provides an anion that is otherwise useful and desirable in the finished detergent composition. For example, citric acid can be used for purposes of neutralization and the resulting citrate ion (ca. 1%) be allowed to remain with a ca. 40% polyhydroxy fatty acid amide slurry and be pumped into the later manufacturing stages of the overall detergent-manufacturing process. The acid forms of materials such as oxydisuccinate, nitrilotriacetate, ethylenediaminetetraacetate, tartrate/succinate, and the like, can be used similarly.

The polyhydroxy fatty acid amides derived from coconut alkyl fatty acids (predominantly C₁₂-C₁₄) are more soluble than their tallow alkyl (predominantly C₁₆-C₁₈) counterparts. Accordingly, the C₁₂-C₁₄ materials are somewhat easier to formulate in liquid compositions, and are more soluble in cool-water laundering baths. However, the C₁₆-C₁₈ materials are also quite useful, especially under circumstances where warm-to-hot wash water is used. Indeed, the C₁₆-C₁₈ materials may be better deterative surfactants than their C₁₂-C₁₄ counterparts. Accordingly, the formulator may wish to balance ease-of-manufacture vs. performance when selecting a particular polyhydroxy fatty acid amide for use in a given formulation.

It will also be appreciated that the solubility of the polyhydroxy fatty acid amides can be increased by having points of unsaturation and/or chain branching in the fatty acid moiety. Thus, materials such as the polyhydroxy fatty acid amides derived from oleic acid and iso-stearic acid are more soluble than their n-alkyl counterparts.

Likewise, the solubility of polyhydroxy fatty acid amides prepared from disaccharides, trisaccharides, etc., will ordinarily be greater than the solubility of their monosaccharide-derived counterpart materials. This higher solubility can be of particular assistance when formulating liquid compositions. Moreover, the polyhydroxy fatty acid amides wherein the polyhydroxy group is derived from maltose appear to function especially well as detergents when used in combination with conventional alkylbenzene

5 sulfonate ("LAS") surfactants. While not intending to be limited by theory, it appears that the combination of LAS with the polyhydroxy fatty acid amides derived from the higher saccharides such as maltose causes a substantial and unexpected lowering of interfacial tension in aqueous media, thereby enhancing net detergency performance. (The manufacture of a polyhydroxy fatty acid amide derived from maltose is described hereinafter.)

10 The polyhydroxy fatty acid amides can be manufactured not only from the purified sugars, but also from hydrolyzed starches, e.g., corn starch, potato starch, or any other convenient plant-derived starch which contains the mono-, di-, etc. saccharide desired by the formulator. This is of particular importance from the economic standpoint. Thus, "high glucose" corn syrup, "high maltose" corn syrup, etc. can conveniently and economically be used. De-lignified, hydrolyzed cellulose pulp can also provide a raw material source for the polyhydroxy fatty acid amides.

20 As noted above, polyhydroxy fatty acid amides derived from the higher saccharides, such as maltose, lactose, etc., are more soluble than their glucose counterparts. Moreover, it appears that the more soluble polyhydroxy fatty acid amides can help solubilize their less soluble counterparts, to varying degrees. Accordingly, the formulator may elect to use a raw material comprising a high glucose corn syrup, for example, but to select a syrup which contains a modicum of maltose (e.g., 1% or more). The resulting mixture of polyhydroxy fatty acids will, in general, exhibit more preferred solubility properties over a broader range of temperatures and concentrations than would a "pure" glucose-derived polyhydroxy fatty acid amide. Thus, in addition to any economic advantages for using sugar mixtures rather than pure sugar reactants, the polyhydroxy fatty acid amides prepared from mixed sugars can offer very substantial advantages with respect to performance and/or ease-of-formulation. In some instances, however, some loss of grease removal performance (dishwashing) may be noted at fatty acid maltamide levels above about 25% and some loss in sudsing above about 33% (said percentages being the percentage of maltamide-derived polyhydroxy fatty acid amide vs. glucose-derived polyhydroxy fatty acid amide in the mixture). This can vary somewhat, depending on the chain length of the fatty

35

acid moiety. Typically, then, the formulator electing to use such mixtures may find it advantageous to select polyhydroxy fatty acid amide mixtures which contain ratios of monosaccharides (e.g., glucose) to di- and higher saccharides (e.g., maltose) from about 4:1 to about 99:1.

The manufacture of preferred, uncyclized polyhydroxy fatty acid amides from fatty esters and N-alkyl polyols can be carried out in alcohol solvents at temperatures from about 30°C-90°C, preferably about 50°C-80°C. It has now been determined that it may be convenient for the formulator of, for example, liquid detergents to conduct such processes in 1,2-propylene glycol solvent, since the glycol solvent need not be completely removed from the reaction product prior to use in the finished detergent formulation. Likewise, the formulator of, for example, solid, typically granular, detergent compositions may find it convenient to run the process at 30°C-90°C in solvents which comprise ethoxylated alcohols, such as the ethoxylated (EO 3-8) C₁₂-C₁₄ alcohols, such as those available as NEODOL 23 E06.5 (Shell). When such ethoxylates are used, it is preferred that they not contain substantial amounts of unethoxylated alcohol and, most preferably, not contain substantial amounts of mono-ethoxylated alcohol. ("T" designation.)

While methods for making polyhydroxy fatty acid amides *per se* form no part of the invention herein, the formulator can also note other syntheses of polyhydroxy fatty acid amides as described hereinafter.

Typically, the industrial scale reaction sequence for preparing the preferred acyclic polyhydroxy fatty acid amides will comprise: Step 1 - preparing the N-alkyl polyhydroxy amine derivative from the desired sugar or sugar mixture by formation of an adduct of the N-alkyl amine and the sugar, followed by reaction with hydrogen in the presence of a catalyst; followed by Step 2 - reacting the aforesaid polyhydroxy amine with, preferably, a fatty ester to form an amide bond. While a variety of N-alkyl polyhydroxy amines useful in Step 2 of the reaction sequence can be prepared by various art-disclosed processes, the following process is convenient and makes use of economical sugar syrup as the raw material. It is to be understood that, for best results when using such syrup raw materials, the manufacturer should

select syrups that are quite light in color or, preferably, nearly colorless ("water-white").

Preparation of N-Alkyl Polyhydroxy Amine

From Plant-Derived Sugar Syrup

5 I. Adduct Formation - The following is a standard process in which about 420 g of about 55% glucose solution (corn syrup - about 231 g glucose - about 1.28 moles) having a Gardner Color of less than 1 is reacted with about 119 g of about 50% aqueous methylamine (59.5 g of methylamine - 1.92 moles) solution. The
10 methylamine (MMA) solution is purged and shielded with N₂ and cooled to about 10°C, or less. The corn syrup is purged and shielded with N₂ at a temperature of about 10°-20°C. The corn syrup is added slowly to the MMA solution at the indicated reaction temperature as shown. The Gardner Color is measured at
15 the indicated approximate times in minutes.

TABLE 1

Time in Minutes:	<u>10</u>	<u>30</u>	<u>60</u>	<u>120</u>	<u>180</u>	<u>240</u>
<u>Reaction Temp. °C</u>	<u>Gardner Color (Approximate)</u>					
0	1	1	1	1	1	1
20	1	1	1	1	1	1
30	1	1	2	2	4	5
50	4	6	10	-	-	-

As can be seen from the above data, the Gardner Color for the adduct is much worse as the temperature is raised above about 30°C and at about 50°C, the time that the adduct has a Gardner Color below 7 is only about 30 minutes. For longer reaction, and/or
25 holding times, the temperature should be less than about 20°C. The Gardner Color should be less than about 7, and preferably less than about 4 for good color glucamine.

30 When one uses lower temperatures for forming the adduct, the time to reach substantial equilibrium concentration of the adduct is shortened by the use of higher ratios of amine to sugar. With the 1.5:1 mole ratio of amine to sugar noted, equilibrium is reached in about two hours at a reaction temperature of about
35 30°C. At a 1.2:1 mole ratio, under the same conditions, the time is at least about three hours. For good color, the combination of amine:sugar ratio; reaction temperature; and reaction time is selected to achieve substantially equilibrium conversion, e.g.,

more than about 90%, preferably more than about 95%, even more preferably more than about 99%, based upon the sugar, and a color that is less than about 7, preferably less than about 4, more preferably less than about 1, for the adduct.

5 Using the above process at a reaction temperature of less than about 20°C and corn syrups with different Gardner Colors as indicated, the MMA adduct color (after substantial equilibrium is reached in at least about two hours) is as indicated.

TABLE 2

	Gardner Color (Approximate)						
Corn syrup	1	1	1	1+	0	0	0+
Adduct	3	4/5	7/8	7/8	1	2	1

10 As can be seen from the above, the starting sugar material must be very near colorless in order to consistently have adduct that is acceptable. When the sugar has a Gardner Color of about 1, the adduct is sometimes acceptable and sometimes not acceptable. When the Gardner Color is above 1 the resulting adduct is unacceptable. The better the initial color of the sugar, the better is the color of the adduct.

20 II. Hydrogen Reaction - Adduct from the above having a Gardner Color of 1 or less is hydrogenated according to the following procedure.

25 About 539 g of adduct in water and about 23.1 g of United Catalyst G49B Ni catalyst are added to a one liter autoclave and purged two times with 200 psig H₂ at about 20°C. The H₂ pressure is raised to about 1400 psi and the temperature is raised to about 50°C. The pressure is then raised to about 1600 psig and the temperature is held at about 50-55°C for about three hours. The product is about 95% hydrogenated at this point. The temperature is then raised to about 85°C for about 30 minutes and the reaction mixture is decanted and the catalyst is filtered out. The product, after removal of water and MMA by evaporation, is about 95% N-methyl glucamine, a white powder.

35 The above procedure is repeated with about 23.1 g of Raney Ni catalyst with the following changes. The catalyst is washed three times and the reactor, with the catalyst in the reactor, is purged twice with 200 psig H₂ and the reactor is pressurized with H₂ at 1600 psig for two hours, the pressure is released at one hour and

the reactor is repressurized to 1600 psig. The adduct is then pumped into the reactor which is at 200 psig and 20°C, and the reactor is purged with 200 psig H₂, etc., as above.

5 The resulting product in each case is greater than about 95% N-methyl glucamine; has less than about 10 ppm Ni based upon the glucamine; and has a solution color of less than about Gardner 2.

The crude N-methyl glucamine is color stable to about 140°C for a short exposure time.

10 It is important to have good adduct that has low sugar content (less than about 5%, preferably less than about 1%) and a good color (less than about 7, preferably less than about 4 Gardner, more preferably less than about 1).

15 In another reaction, adduct is prepared starting with about 159 g of about 50% methylamine in water, which is purged and shielded with N₂ at about 10-20°C. About 330 g of about 70% corn syrup (near water-white) is degassed with N₂ at about 50°C and is added slowly to the methylamine solution at a temperature of less than about 20°C. The solution is mixed for about 30 minutes to give about 95% adduct that is a very light yellow solution.

20 About 190 g of adduct in water and about 9 g of United Catalyst G49B Ni catalyst are added to a 200 ml autoclave and purged three times with H₂ at about 20°C. The H₂ pressure is raised to about 200 psi and the temperature is raised to about 50°C. The pressure is raised to 250 psi and the temperature is held at about 50-55°C for about three hours. The product, which is about 95% hydrogenated at this point, is then raised to a temperature of about 85°C for about 30 minutes and the product, after removal of water and evaporation, is about 95% N-methyl glucamine, a white powder.

30 It is also important to minimize contact between adduct and catalyst when the H₂ pressure is less than about 1000 psig to minimize Ni content in the glucamine. The nickel content in the N-methyl glucamine in this reaction is about 100 ppm as compared to the less than 10 ppm in the previous reaction.

35 The following reactions with H₂ are run for direct comparison of reaction temperature effects.

A 200 ml autoclave reactor is used following typical procedures similar to those set forth above to make adduct and to run the hydrogen reaction at various temperatures.

- 59 -

5 Adduct for use in making glucamine is prepared by combining about 420 g of about 55% glucose (corn syrup) solution (231 g glucose; 1.28 moles) (the solution is made using 99DE corn syrup from CarGill, the solution having a color less than Gardner 1) and about 119 g of 50% methylamine (59.5 g MMA; 1.92 moles) (from Air Products).

The reaction procedure is as follows:

- 10 1. Add about 119 g of the 50% methylamine solution to a N₂ purged reactor, shield with N₂ and cool down to less than about 10°C.
2. Degas and/or purge the 55% corn syrup solution at 10-20°C with N₂ to remove oxygen in the solution.
3. Slowly add the corn syrup solution to the methylamine solution and keep the temperature less than about 20°C.
- 15 4. Once all corn syrup solution is added in, agitate for about 1-2 hours.

The adduct is used for the hydrogen reaction right after making, or is stored at low temperature to prevent further degradation.

20 The glucamine adduct hydrogen reactions are as follows:

1. Add about 134 g adduct (color less than about Gardner 1) and about 5.8 g G49B Ni to a 200 ml autoclave.
 2. Purge the reaction mix with about 200 psi H₂ twice at about 20-30°C.
 - 25 3. Pressure with H₂ to about 400 psi and raise the temperature to about 50°C.
 4. Raise pressure to about 500 psi, react for about 3 hours. Keep temperature at about 50-55°C. Take Sample 1.
 5. Raise temperature to about 85°C for about 30 minutes.
 - 30 6. Decant and filter out the Ni catalyst. Take Sample 2.
- Conditions for constant temperature reactions:
1. Add about 134 g adduct and about 5.8 g G49B Ni to a 200 ml autoclave.
 2. Purge with about 200 psi H₂ twice at low temperature.
 - 35 3. Pressure with H₂ to about 400 psi and raise temperature to about 50°C.
 4. Raise pressure to about 500 psi, react for about 3.5 hours. Keep temperature at indicated temperature.

- 60 -

5. Decant and filter out the Ni catalyst. Sample 3 is for about 50-55°C; Sample 4 is for about 75°C; and Sample 5 is for about 85°C. (The reaction time for about 85°C is about 45 minutes.)

5 All runs give similar purity of N-methyl glucamine (about 94%); the Gardner Colors of the runs are similar right after reaction, but only the two-stage heat treatment gives good color stability; and the 85°C run gives marginal color immediately after reaction.

10

EXAMPLE 17

The preparation of the tallow (hardened) fatty acid amide of N-methyl maltamine for use in detergent compositions according to this invention is as follows.

15 Step 1 - Reactants: Maltose monohydrate (Aldrich, lot 01318KW); methylamine (40 wt% in water) (Aldrich, lot 03325TM); Raney nickel, 50% slurry (UAD 52-73D, Aldrich, lot 12921LW).

20 The reactants are added to glass liner (250 g maltose, 428 g methylamine solution, 100 g catalyst slurry - 50 g Raney Ni) and placed in 3 L rocking autoclave, which is purged with nitrogen (3X500 psig) and hydrogen (2X500 psig) and rocked under H₂ at room temperature over a weekend at temperatures ranging from 28°C to 50°C. The crude reaction mixture is vacuum filtered 2X through a glass microfiber filter with a silica gel plug. The filtrate is concentrated to a viscous material. The final traces of water are
25 azetroped off by dissolving the material in methanol and then removing the methanol/water on a rotary evaporator. Final drying is done under high vacuum. The crude product is dissolved in refluxing methanol, filtered, cooled to recrystallize, filtered and the filter cake is dried under vacuum at 35°C. This is cut
30 #1. The filtrate is concentrated until a precipitate begins to form and is stored in a refrigerator overnight. The solid is filtered and dried under vacuum. This is cut #2. The filtrate is again concentrated to half its volume and a recrystallization is performed. Very little precipitate forms. A small quantity of
35 ethanol is added and the solution is left in the freezer over a weekend. The solid material is filtered and dried under vacuum. The combined solids comprise N-methyl maltamine which is used in Step 2 of the overall synthesis.

- 61 -

Step 2 - Reactants: N-methyl maltamine (from Step 1); hardened tallow methyl esters; sodium methoxide (25% in methanol); absolute methanol (solvent); mole ratio 1:1 amine:ester; initial catalyst level 10 mole % (w/r maltamine), raised to 20 mole %; solvent level 50% (wt.).

In a sealed bottle, 20.36 g of the tallow methyl ester is heated to its melting point (water bath) and loaded into a 250 ml 3-neck round-bottom flask with mechanical stirring. The flask is heated to ca. 70°C to prevent the ester from solidifying. Separately, 25.0 g of N-methyl maltamine is combined with 45.36 g of methanol, and the resulting slurry is added to the tallow ester with good mixing. 1.51 g of 25% sodium methoxide in methanol is added. After four hours the reaction mixture has not clarified, so an additional 10 mole % of catalyst (to a total of 20 mole %) is added and the reaction is allowed to continue overnight (ca. 68°C) after which time the mixture is clear. The reaction flask is then modified for distillation. The temperature is increased to 110°C. Distillation at atmospheric pressure is continued for 60 minutes. High vacuum distillation is then begun and continued for 14 minutes, at which time the product is very thick. The product is allowed to remain in the reaction flask at 110°C (external temperature) for 60 minutes. The product is scraped from the flask and triturated in ethyl ether over a weekend. Ether is removed on a rotary evaporator and the product is stored in an oven overnight, and ground to a powder. Any remaining N-methyl maltamine is removed from the product using silica gel. A silica gel slurry in 100% methanol is loaded into a funnel and washed several times with 100% methanol. A concentrated sample of the product (20 g in 100 ml of 100% methanol) is loaded onto the silica gel and eluted several times using vacuum and several methanol washes. The collected eluant is evaporated to dryness (rotary evaporator). Any remaining tallow ester is removed by trituration in ethyl acetate overnight, followed by filtration. The filter cake is vacuum dried overnight. The product is the tallowalkyl N-methyl maltamide.

In an alternate mode, Step 1 of the foregoing reaction sequence can be conducted using commercial corn syrup comprising glucose or mixtures of glucose and, typically, 5%, or higher,

- 62 -

maltose. The resulting polyhydroxy fatty acid amides and mixtures can be used in any of the detergent compositions herein.

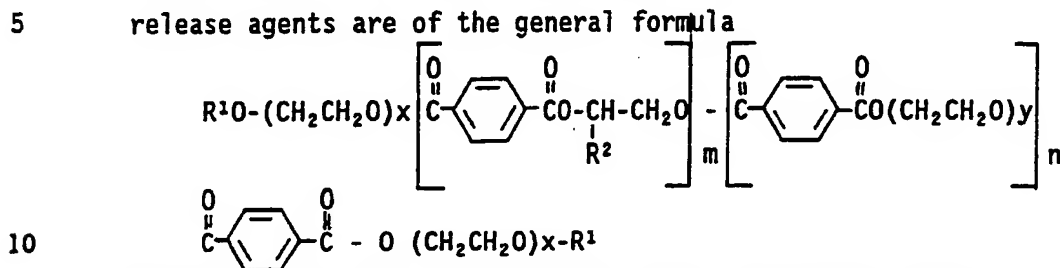
5 In still another mode, Step 2 of the foregoing reaction sequence can be carried out in 1,2-propylene glycol or NEODOL. At the discretion of the formulator, the propylene glycol or NEODOL need not be removed from the reaction product prior to its use to formulate detergent compositions. Again, according to the desires of the formulator, the methoxide catalyst can be neutralized by citric acid to provide sodium citrate, which can remain in the
10 polyhydroxy fatty acid amide.

Depending on the desires of the formulator, the compositions herein can contain more or less of various suds control agents. Typically, for dishwashing high sudsing is desirable so no suds control agent will be used. For fabric laundering in top-loading
15 washing machines some control of suds may be desirable, and for front-loaders some considerable degree of suds control may be preferred. A wide variety of suds control agents are known in the art and can be routinely selected for use herein. Indeed, the selection of suds control agent, or mixtures of suds control agents, for any specific detergent composition will depend not only on the presence and amount of polyhydroxy fatty acid amide used therein, but also on the other surfactants present in the formulation. However, it appears that, for use with polyhydroxy
20 fatty acid amides, silicone-based suds control agents of various types are more efficient (i.e., lower levels can be used) than various other types of suds control agents. The silicone suds control agents available as X2-3419 and Q2-3302 (Dow Corning) are particularly useful herein.

The formulator of fabric laundering compositions which can
30 advantageously contain soil release agent has a wide variety of known materials to choose from (see, for example, U.S. Patents 3,962,152; 4,116,885; 4,238,531; 4,702,857; 4,721,580 and 4,877,896). Additional soil release materials useful herein include the nonionic oligomeric esterification product of a
35 reaction mixture comprising a source of C₁-C₄ alkoxy-terminated polyethoxy units (e.g., CH₃[OCH₂CH₂]₁₆OH), a source of terephthaloyl units (e.g., dimethyl terephthalate); a source of poly(oxyethylene)oxy units (e.g., polyethylene glycol 1500); a

- 63 -

source of oxyiso-propyleneoxy units (e.g., 1,2-propylene glycol); and a source of oxyethyleneoxy units (e.g., ethylene glycol) especially wherein the mole ratio of oxyethyleneoxy units:oxyiso-propyleneoxy units is at least about 0.5:1. Such nonionic soil release agents are of the general formula



wherein R^1 is lower (e.g., $\text{C}_1\text{-C}_4$) alkyl, especially methyl; x and y are each integers from about 6 to about 100; m is an integer of from about 0.75 to about 30; n is an integer from about 0.25 to about 20; and R^2 is a mixture of both H and CH_3 to provide a mole ratio of oxyethyleneoxy:oxyisopropyleneoxy of at least about 0.5:1.

Another preferred type of soil release agent useful herein is of the general anionic type described in U.S. Patent 4,877,896, but with the condition that such agents be substantially free of monomers of the HOROH type wherein R is propylene or higher alkyl. Thus, the soil release agents of U.S. Patent 4,877,896 can comprise, for example, the reaction product of dimethyl terephthalate, ethylene glycol, 1,2-propylene glycol and 3-sodiosulfobenzoic acid, whereas these additional soil release agents can comprise, for example, the reaction product of dimethyl terephthalate, ethylene glycol, 5-sodiosulfoisophthalate and 3-sodiosulfobenzoic acid. Such agents are preferred for use in granular laundry detergents.

The formulator may also determine that it is advantageous to include a non-perborate bleach, especially in heavy-duty granular laundry detergents. A variety of peroxygen bleaches are available, commercially, and can be used herein, but, of these, percarbonate is convenient and economical. Thus, the compositions herein can contain a solid percarbonate bleach, normally in the form of the sodium salt, incorporated at a level of from 3% to 20% by weight, more preferably from 5% to 18% by weight and most preferably from 8% to 15% by weight of the composition.

- 64 -

Sodium percarbonate is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. Most commercially available material includes a low level of a heavy metal sequestrant such as EDTA, 1-hydroxyethylidene 1,1-diphosphonic acid (HEDP) or an amino-phosphonate, that is incorporated during the manufacturing process. For use herein, the percarbonate can be incorporated into detergent compositions without additional protection, but preferred embodiments of the invention utilize a stable form of the material (FMC). Although a variety of coatings can be used, the most economical is sodium silicate of $\text{SiO}_2:\text{Na}_2\text{O}$ ratio from 1.6:1 to 2.8:1, preferably 2.0:1, applied as an aqueous solution and dried to give a level of from 2% to 10% (normally from 3% to 5%), of silicate solids by weight of the percarbonate. Magnesium silicate can also be used and a chelant such as one of those mentioned above can also be included in the coating.

The particle size range of the crystalline percarbonate is from 350 micrometers to 450 micrometers with a mean of approximately 400 micrometers. When coated, the crystals have a size in the range from 400 to 600 micrometers.

While heavy metals present in the sodium carbonate used to manufacture the percarbonate can be controlled by the inclusion of sequestrants in the reaction mixture, the percarbonate still requires protection from heavy metals present as impurities in other ingredients of the product. It has been found that the total level of iron, copper and manganese ions in the product should not exceed 25 ppm and preferably should be less than 20 ppm in order to avoid an unacceptably adverse effect on percarbonate stability.

The following relates to the preparation of a preferred liquid heavy duty laundry detergent according to this invention. It will be appreciated that the stability of enzymes in such compositions is considerably less than in granular detergents. However, by using typical enzyme stabilizers such as formate and boric acid, lipase and cellulase enzymes can be protected from degradation by protease enzymes. However, lipase stability is still relatively poor in the presence of alkylbenzene sulfonate ("LAS") surfactants. Apparently, LAS partially denatures lipase,

and, further, it seems that denatured lipase is more vulnerable to attack by protease.

5 In view of the foregoing considerations, which, as noted, can be particularly troublesome in liquid compositions, it is a challenge to provide liquid detergent compositions containing lipase, protease and cellulase enzymes, together. It is particularly challenging to provide such tertiary enzyme systems in stable liquid detergents together with an effective blend of
10 deterative surfactants. Additionally, it is difficult to incorporate peroxidase and/or amylase enzymes stably in such compositions.

It has now been determined that various mixtures of lipases, proteases, cellulases, amylases and peroxidases are adequately stable in the presence of certain non-alkylbenzene sulfonate
15 surfactant systems, such that effective, heavy-duty solid and even liquid detergents can be formulated. Indeed, the formulation of stable, liquid, enzyme-containing detergent compositions constitutes a highly advantageous and preferred embodiment afforded by the technology of the present invention.

20 In particular, prior art liquid detergent compositions typically contain LAS or mixtures of LAS with surfactants of the $RO(A)_mSO_3M$ type ("AES") noted hereinabove, i.e., LAS/AES mixtures. By contrast, the liquid detergents herein preferably comprise binary mixtures of the AES and polyhydroxy fatty acid amides of the type disclosed herein. While minimal amounts of LAS can be
25 present, it will be appreciated that the stability of the enzymes will be lessened thereby. Accordingly, it is preferred that the liquid compositions be substantially free (i.e., contain less than about 10%, preferably less than about 5%, more preferably less than about 1%, most preferably 0%) of LAS.
30

The present invention provides a liquid detergent composition comprising:

- (a) from about 1% to about 50%, preferably from about 4% to about 40%, of anionic surfactant;
- 35 (b) from about 0.0001% to about 2% of active deterative enzyme;

- 66 -

- (c) an enzyme performance-enhancing amount (preferably from about 0.5% to about 12%) of a polyhydroxy fatty acid amide material of the formula



wherein R¹ is H₁, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, R₂ is C₅-C₃₁ hydrocarbyl, and Z is a polyhydroxylhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to said chain, or an alkoxylated derivative thereof;

- (d) a nonionic surfactant, especially about 1%-20% of an alkoxylated C₁₂-C₁₈ alcohol with 3-10 EO groups; and wherein the composition is substantially free of alkylbenzene sulfonate.

The water-soluble anionic surfactant herein preferably comprises ("AES"):



wherein R is an unsubstituted C₁₀-C₂₄ alkyl or hydroxyalkyl (C₁₀-C₂₄) group, A is an ethoxy or propoxy unit, m is an integer greater than 0 and M is hydrogen or a cation. Preferably, R is an unsubstituted C₁₂-C₁₈ alkyl group, A is an ethoxy unit, m is from about 0.5 to about 6, and M is a cation. The cation is preferably a metal cation (e.g., sodium-preferred, potassium, lithium, calcium, magnesium, etc.) or an ammonium or substituted ammonium cation.

It is preferred that the ratio of the above surfactant ("AES") to the polyhydroxy fatty acid amide herein be from about 1:2 to about 8:1, preferably about 1:1 to about 5:1, most preferably about 1:1 to about 4:1.

The liquid compositions herein may alternatively comprise polyhydroxy fatty acid amide, AES, and from about 0.5% to about 5% of the condensation product of C₈-C₂₂ (preferably C₁₀-C₂₀) linear alcohol with between about 1 and about 25, preferably between about 2 and about 18, moles of ethylene oxide per mole of alcohol.

As described above, the liquid compositions herein preferably have a pH in a 10% solution in water at 20°C of from about 6.5 to about 11.0, preferably from about 7.0 to about 8.5.

5 The instant compositions preferably further comprise from about 0.1% to about 50% of detergency builder. These compositions preferably comprise from about 0.1% to about 20% of citric acid, or water-soluble salt thereof, and from about 0.1% to about 20% of a water-soluble succinate tartrate, especially the sodium salt thereof, and mixtures thereof, or from about 0.1% to about 20% by weight of oxydisuccinate or mixtures thereof with the aforesaid builders. 0.1%-50% of alkenyl succinate can also be used.

10 The preferred liquid compositions herein comprise from about 0.0001% to about 2%, preferably about 0.0001% to about 1%, most preferably about 0.001% to about 0.5%, on an active basis, of deterative enzyme. These enzymes are preferably selected from the group consisting of protease (preferred), lipase (preferred), amylase, cellulase, peroxidase, and mixtures thereof. Preferred
15 are compositions with two or more classes of enzymes, most preferably where one is a protease.

While various descriptions of detergent proteases, cellulases, etc., are available in the literature, detergent lipases may be somewhat less familiar. Accordingly, to assist the formulator, lipases of interest include Amano AKG and Bacillis Sp lipase (e.g., Solvay enzymes). Also, see the lipases described in
20 EP A 0 399 681, published November 28, 1990, EP A 0 218 272, published April 15, 1987 and PCT/DK 88/00177, published May 18, 1989, all incorporated herein by reference.

25 Suitable fungal lipases include those producible by *Humicola lanuginosa* and *Thermomyces lanuginosus*. Most preferred is the lipase obtained by cloning the gene from *Humicola lanuginosa* and expressing the gene in *Aspergillus oryzae*, as described in European Patent Application 0 258 068, incorporated herein by reference, commercially available under the trade name LIPOLASE.
30

From about 2 to about 20,000, preferably about 10 to about 6,000, lipase units of lipase per gram (LU/g) of product can be used in these compositions. A lipase unit is that amount of lipase which produces 1 μ mol of titratable butyric acid per minute
35 in a pH stat, where pH is 7.0, temperature is 30°C, and substrate is an emulsion tributyrin and gum arabic, in the presence of Ca⁺⁺ and NaCl in phosphate buffer.

EXAMPLES 18 A-C

The following Examples illustrate light duty liquid detergent compositions which are especially adapted for dishwashing and other hard surface cleaning operations. In the Examples A-C, the surfactants comprise various alkyl ethoxy sulfate surfactants which, using standard terminology, are abbreviated to indicate their average degree of ethoxylation; thus C₁₂₋₁₃EO(0.8) sulfate indicates a sulfated mixed C₁₂-C₁₃ alcohol fraction having an average degree of ethoxylation of 0.8. These anionic ethoxy sulfates are preferably used in their Na⁺ or NH₄⁺ salt form. The C₁₂₋₁₃ amine oxide is a mixed C₁₂₋₁₃ (average) dimethyl amine oxide. The C₁₂₋₁₄ AP betaine is C_{12/14}H_{25/29}CONH(CH₂)₃N⁺(CH₃)₂-CH₂CO₂H. The C₁₂₋₁₄ AP sultaine is C_{12/14}H_{25/29}CONH(CH₂)₃N⁺-(CH₃)₂CH₂CH(OH)CH₂SO₃H. The C₁₂₋₁₄ DM betaine is C_{12/14}H_{25/29}N⁺-(CH₃)₂CH₂CO₂H. The ethoxylated nonionic surfactant designated C₉₋₁₁EO(8) refers to C₉-C₁₁ alcohols ethoxylated with an average of 8 moles of ethylene oxide. The Ca⁺⁺ and Mg⁺⁺ cations are conveniently introduced into the compositions as CaCl₂ and MgCl₂. The balance of the compositions comprises water and citrate/propylene glycol present in the glucamide surfactant (1-5%) and 1-3% cumene sulfonate or xylene sulfonate hydrotrope. The pH is typically 6.8-7.4 (NH₄⁺ salts) or 7-8.2 (Na⁺ salts).

	<u>Ingredient</u>	<u>Percent (wt.)</u>		
		<u>A</u>	<u>B</u>	<u>C</u>
25	C ₁₂₋₁₄ N-methyl glucamide	11	8	12.7
	C ₁₂₋₁₃ EO(0.8) sulfate	--	16	10.0
	C ₁₂₋₁₄ EO(3) sulfate	11	--	2.7
	C ₁₂₋₁₃ EO(6.5) sulfate	--	--	--
	C ₁₂₋₁₄ AP betaine	--	--	2
30	C ₁₂₋₁₄ AP sultaine	--	--	--
	C ₁₂₋₁₃ amine oxide	2.5	--	--
	C ₁₂₋₁₄ DM betaine	--	2.0	--
	C ₉₋₁₁ EO(8)	0.5	8	7
	Ca ⁺⁺	--	--	0.5
35	Mg ⁺⁺	0.9	0.25	--
	Balance	Bal	Bal	Bal

- 69 -

EXAMPLE 19

A liquid laundry detergent composition suitable for use at the relatively high concentrations common to front-loading automatic washing machines, especially in Europe, and over a wide range of temperatures is as follows.

	<u>Ingredient</u>	<u>Wt. %</u>
	Coconutalkyl (C ₁₂) N-methyl glucamide	14
	C ₁₄₋₁₅ EO(2.25) sulfate, Na salt	10.0
	C ₁₄₋₁₅ EO(7)	4.0
10	C ₁₂₋₁₄ alkenylsuccinic anhydride ¹	4.0
	C ₁₂₋₁₄ fatty acid*	3.0
	Citric acid (anhydrous)	4.6
	Protease (enzyme) ²	0.37
	Termamyl (enzyme) ³	0.12
15	Lipolase (enzyme) ⁴	0.36
	Carezyme (enzyme) ⁵	0.12
	Dequest 2060S ⁶	1.0
	NaOH (pH to 7.6)	5.5
	1,2 propanediol	4.7
20	Ethanol	4.0
	Sodium metaborate	4.0
	CaCl ₂	0.014
	Ethoxylated tetraethylene pentamine ⁷	0.4
	Brightener ⁸	0.13
25	Silane ⁹	0.04
	Soil release polymer ¹⁰	0.2
	Silicone (suds control) ¹¹	0.4
	Silicone dispersant ¹²	0.2
	Water and minors	Balance

30 ¹As SYNPRAX 3 from ICI or DTSA from Monsanto.

²As Protease B as described in EPO 0342177 November 15, 1989, percentage at 40 g/l.

³Amylase, from NOVO; percentage at 300 KNU/g.

⁴Lipase, from NOVO; percentage at 100 KLU/g.

35 ⁵Cellulase from NOVO; percentage at 5000 CEVU/l.

⁶Available from Monsanto.

⁷From BASF as LUTENSOL P6105.

⁸BLANKOPHOR CPG766, Bayer.

- 70 -

⁹Silane corrosion inhibitor, available as A1130 from Union Carbide or DYNASYLAN TRIAMINO from H&I.

¹⁰Polyester, per U.S. Patent 4,711,730.

¹¹Silicone suds control agent available as Q2-3302 from Dow
5 Corning.

¹²Dispersant for silicone suds control agent available as DC-3225C from Dow Corning.

*Preferred fatty acid is topped palm kernel, comprising 12% oleic and 2% each of stearic and linoleic.

10

EXAMPLE 20

A granular laundry detergent composition suitable for use at the relatively high concentrations common to front-loading automatic washing machines, especially in Europe, and over a wide range of temperatures is as follows.

15	<u>Ingredient</u>	<u>Wt. %</u>
	SOKALAN CP5 (100% active as Na salt) ¹	3.52
	DEQUEST 2066 (100% as acid) ²	0.45
	TINOPAL DMS ³	0.28
	MgSO ₄	0.49
20	Zeolite A (anhydrous 2-5 μ)	17.92
	CMC (100% active) ⁴	0.47
	Na ₂ CO ₃	9.44
	Citric acid	3.5
	Layered Silicate SKS-6	12.9
25	Tallow alkyl sulfate (100% active; Na salt)	2.82
	C ₁₄ -C ₁₅ alkyl sulfate (100% active; Na salt)	3.5
	C ₁₂ -C ₁₅ alkyl EO(3) sulfate	1.76
	C ₁₆ -C ₁₈ N-methyl glucamide	4.1
	DOBANOL C ₁₂ -C ₁₅ EO(3)	3.54
30	LIPOLASE (100,000 LU/g) ⁵	0.42
	SAVINASE (4.0 KNPU) ⁶	1.65
	Perfume	0.53
	X2-3419 ⁷	0.22
	Starch	1.08
35	Stearyl alcohol	0.35
	Sodium percarbonate (coated)	22.3
	Tetraacetylenediamine (TAED)	5.9

- 71 -

Zinc phthalocyanin	0.02
Water (ex zeolite)	Balance

¹SOKALAN is sodium poly-acrylate/maleate available from Hoechst.

5 ²Monsanto brand of pentaphosphonomethyl diethylenetriamine.

³Optical brightener available from Ciba Geigy.

⁴Trade name FINNFIK available from Metasaliton.

⁵LIPOLASE lipolytic enzyme from NOVO.

⁶SAVINASE protease enzyme from NOVO.

10 ⁷X2-3419 is a silicone suds suppressor available from Dow Corning.

The procedure for preparing the granules comprises various tower-drying, agglomerating, dry-additions, etc., as follows. The percentages are based on the finished composition.

15 A. Crutched and Blown Through the Tower

Using standard techniques the following components are crutched and tower-dried.

	SOKALAN CP5	3.52%
	DEQUEST 2066	0.45%
20	TINOPAL DMS	0.28%
	Magnesium sulfate	0.49%
	ZEOLITE A as anhydrous	7.1%
	CMC	0.47%

B. Surfactant Agglomerates

25 B1. Agglomeration of Sodium Salt of Tallow Alkyl Sulfate and Sodium Salt of C₁₂₋₁₅ EO(3) Sulfate Pastes - A 50% active paste of tallow alkyl sulfate and a 70% paste of C_{12-C₁₅} EO(3) sulfate are agglomerated with Zeolite A and sodium carbonate according to the following formula (contribution to the detergent formulation after the drying of the agglomerate).

30	Tallow alkyl sulfate	2.82%
	C ₁₂₋₁₅ EO(3) sulfate	1.18%
	Zeolite A	5.3%
	Sodium carbonate	4.5%

35 B2. Agglomerate of the C_{14-C₁₅} Alkyl Sulfate, C_{12-C₁₅} Alkyl Ethoxy Sulfate, DOBANOL C_{12-C₁₅} EO(3) and C_{16-C₁₈} N-methyl glucose amide - The C_{16-C₁₈} glucose amide nonionic material is synthesized with DOBANOL C₁₂₋₁₅EO(3) present during the reaction of methyl

- 72 -

ester and N-methyl glucamine. The C₁₂₋₁₅EO(3) acts as a melting point depressor which allows the reaction to be run without forming cyclic glucose amides which are undesirable.

5 A surfactant mixture of 20% DOBANOL C₁₂₋₁₅ EO(3) and 80% C₁₆-C₁₈ N-methyl glucose amide is obtained and coagglomerated with 10% sodium carbonate.

Second, the above particle is then coagglomerated with a high active paste (70%) of a sodium salt of C₁₄-C₁₅ alkyl sulfate and C₁₂₋₁₅ EO(3) sulfate and Zeolite A and extra sodium carbonate.
10 This particle evidences a good dispersibility in cold water of the C₁₆-C₁₈ N-methyl glucose amide.

The overall formulation of this particle (contribution to the detergent formulation after the drying of the agglomerate) is:

	C ₁₆ -C ₁₈ N-methyl glucose amide	4.1%
15	DOBANOL C ₁₂₋₁₅ EO(3)	0.94%
	Sodium carbonate	4.94%
	Zeolite A	5.3%
	Na C ₁₄ -C ₁₅ alkyl sulfate	3.5%
	Na C ₁₂₋₁₅ EO(3) sulfate	0.59%

20 C. Dry Additives

The following ingredients are added.

	Percarbonate	22.3%
	TAED (tetraacetylenediamine)	5.9%
	Layered silicate SKS 6 from Hoechst	12.90%
25	Citric acid	3.5%
	Lipolase	0.42%
		100,000 LU/g
	SAVINASE 4.0 KNPU	1.65%
	Zinc phthalocyanin (photobleach)	0.02%

30 D. Spray on

	DOBANOL C ₁₂₋₁₅ EO(3)	2.60%
	Perfume	0.53%

E. Suds Suppressor

35 The silicone suds suppressor X2-3419 (95%-97% high molecular weight starch; 3%-5% hydrophobic silica) ex Dow Corning is coagglomerated with Zeolite A (2-5 μ size), starch and stearyl alcohol binder. This particle has the following formulation:

- 73 -

Zeolite A	0.22%
Starch	1.08%
X2-3419	0.22%
Stearyl alcohol	0.35%

5 The detergent preparation exhibits excellent solubility, superior performance and excellent suds control when used in European washing machine, e.g., using 85 g detergent in a AEG-brand washing machine in 30°C, 40°C, 60°C and 90°C cycles.

EXAMPLE 21

10 In any of the foregoing examples, the fatty acid glucamide surfactant can be replaced by an equivalent amount of the malt-amide surfactant, or mixtures of glucamide/maltamide surfactants derived from plant sugar sources. In the compositions the use of ethanolamides appears to help cold temperature stability of the
15 finished formulations. Moreover, the use of sulfobetaine (aka "sultaine") surfactants provides superior sudsing.

 The following Examples illustrate further liquid compositions (both Mg^{++} and Ca^{++} , as noted above) which are especially suitable for "light-duty" use, such as for dishwashing.

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EXAMPLE 22 A-D

	<u>Ingredients</u>	<u>Percent (wt.)</u>			
		<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
	C_{12-14} alkyl ethoxy sulfate (1 EO)	16	9	12	--
	C_{12-14} alkyl ethoxy sulfate (3 EO)	--	14	--	11
25	C_{10} alkyl ethoxylate (8EO)	7	3	7	1
	C_{12-14} N-methyl glucamide	8	9	12	6
	Coconut diethanolamide	--	--	--	5
	Dimethyl dodecyl amine oxide	--	1	--	2
	Cocoamidopropyl hydroxysultaine	--	1	3	--
30	Cocoamidopropyl betaine	2	--	--	--
	Mg^{2+}	--	--	1	1
	Ca^{2+}	0.5	1	--	--
	Sodium toluene sulfonate	3	3	3	3
	Ethanol	4	4	4	4
35	Water	----- Balance -----			

 In the event that especially high sudsing compositions are desired (e.g., dishwashing), it is preferred that less than about

- 74 -

5 5%, more preferably less than about 2%, most preferably substantially no C₁₄ or higher fatty acids be present, since these can suppress sudsing. Accordingly, the formulator of high sudsing compositions will desirably avoid the introduction of suds-suppressing amounts of such fatty acids into high sudsing compositions with the polyhydroxy fatty acid amides, and/or avoid the formation of C₁₄ and higher fatty acids on storage of the finished compositions. One simple means is to use C₁₂ ester reactants to prepare the polyhydroxy fatty acid amides herein. Fortunately, 10 the use of amine oxide or sulfobetaine surfactants can overcome some of the negative sudsing effects caused by the fatty acids.

The formulator wishing to add anionic optical brighteners to liquid detergents containing relatively high concentrations (e.g., 10% and greater) of anionic or polyanionic substituents such as the 15 polycarboxylate builders may find it useful to pre-mix the brightener with water and the polyhydroxy fatty acid amide, and then to add the pre-mix to the final composition.

Polyglutamic acid or polyaspartic acid dispersants can be usefully employed with zeolite-built detergents. AE fluid or flake 20 and DC-544 (Dow Corning) are other examples of useful suds control agents herein.

It will be appreciated by those skilled in the chemical arts that the preparation of the polyhydroxy fatty acid amides herein using the di- and higher saccharides such as maltose will result in 25 the formation of polyhydroxy fatty acid amides wherein linear substituent Z is "capped" by a polyhydroxy ring structure. Such materials are fully contemplated for use herein and do not depart from the spirit and scope of the invention as disclosed and claimed.

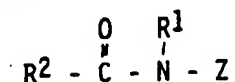
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CLAIMS

1. A nonionic surfactant system characterized in that it comprises:

- (a) one or more polyhydroxy fatty acid amides having the formula



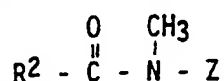
wherein R^1 is H, a C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or mixtures thereof, R^2 is a C_5 - C_{31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyl groups directly connected to the chain, or an alkoxylated derivative thereof; and

- (b) one or more additional nonionic surfactants;

wherein the weight ratio of polyhydroxy fatty acid amide (a) to additional nonionic surfactant (b) is in the range of from 1:5 to 5:1.

2. A nonionic surfactant system according to Claim 1 wherein R^1 is a C_1 - C_2 alkyl group and R^2 is a C_9 - C_{17} alkyl or alkenyl group.

3. A nonionic surfactant system according to Claim 2 wherein the polyhydroxy fatty acid amide component (a) has the formula



wherein R^2 is a C_{11} - C_{17} straight-chain alkyl or alkenyl group, and Z is derived from glucose, maltose or mixtures thereof.

4. A nonionic surfactant system according to Claim 2 wherein the additional nonionic surfactant (b) is selected from the group consisting of polyethylene oxide condensates of alkyl phenols, the condensation products of primary and secondary aliphatic alcohols with from 1 to 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof.

5. A nonionic surfactant system according to Claim 4 wherein the weight ratio of polyhydroxy fatty acid amide (a) to additional nonionic surfactant (b) is in the range of from 1:3 to 3:1.

6. A nonionic surfactant system according to Claim 5 wherein the additional nonionic surfactant (b) is selected from a C₈-C₁₄ alkyl phenol ethoxylate having from 3 to 15 ethoxy groups, a C₁₂-C₁₈ alcohol ethoxylate having from 2 to 10 ethoxy groups, and mixtures thereof.

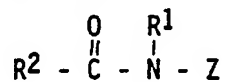
7. A nonionic surfactant system according to Claim 1 which is substantially free of suds-suppressing amounts of C₁₄ and higher fatty acids.

8. A nonionic surfactant system according to Claim 1 wherein, with respect to said polyhydroxy fatty acid amide, Z is derived from maltose.

9. A nonionic surfactant system according to Claim 1 wherein, with respect to said polyhydroxy fatty acid amide, Z is derived from a mixture of monosaccharides, disaccharides and, optionally, higher saccharides, said mixture comprising at least 1% of at least one disaccharide, preferably maltose.

10. A laundry detergent composition comprising at least 1% by weight of a nonionic surfactant system characterized in that it comprises:

- (a) one or more polyhydroxy fatty acid amides having the formula

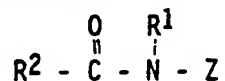


wherein R¹ is H, a C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or mixtures thereof, R² is a C₅-C₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyl groups directly connected to the chain, or an alkoxylated derivative thereof; and

- (b) one or more additional nonionic surfactants; wherein the weight ratio of polyhydroxy fatty acid amide (a) to additional nonionic surfactant (b) is in the range of from 1:5 to 5:1.

11. A laundry detergent composition according to Claim 10 which further comprises a surfactant selected from one or more anionic, cationic, ampholytic, zwitterionic, semi-polar, and optional nonionic surfactants, and mixtures thereof.

12. A method for improving stain removing performance of a detergent composition comprising one or more nonionic deterative surfactants and optional detergent adjuncts, characterized in that said improvement comprises: incorporating into said detergent composition a nonionic surfactant system comprising: one or more polyhydroxy fatty acid amides having the formula



wherein R^1 is H, a C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or mixtures thereof, R^2 is a C_5 - C_{31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyl groups directly connected to the chain, preferably C_{11} - C_{17} N-methyl glucamide, C_{11} - C_{17} N-methyl maltamide, or mixtures of said glucamide and maltamide, or an alkoxyated derivative thereof; and one or more additional nonionic surfactants; wherein the weight ratio of polyhydroxy fatty acid amide to additional nonionic surfactant is in the range of from 1:5 to 5:1.

13. A method according to Claim 12 wherein said Z moiety in said polyhydroxy fatty acid amide is derived from mixed monosaccharides, disaccharides and polysaccharides available from plant sources.

14. A method according to Claim 12 wherein said R^2 moiety in said polyhydroxy fatty acid amide is C_{15} - C_{17} alkyl, alkenyl, or mixtures thereof.

15. A method for removing stains from fabrics, characterized in that said fabrics are contacted with a detergent composition whose stain removing performance has been enhanced by the method of Claim 12.

16. A dishwashing composition with enhanced sudsing containing a nonionic surfactant system according to Claim 7.

INTERNATIONAL SEARCH REPORT

PCT/US 91/06980

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C11D1/835; C11D1/52; C11D3/32		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification Systems	Classification Symbols	
Int.Cl. 5	C11D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 285 768 (HULS AG) 12 October 1988 cited in the application	1-4, 8, 9
A	see page 2, line 1 - page 3, line 17; claims 1-4 ---	10-16
X	US,A,3 312 627 (D.T. HOOKER) 4 April 1967 cited in the application see column 4, line 8 - line 27 see column 5, line 1 - line 20; claim 1 ---	1-4
A	US,A,2 965 576 (E.R. WILSON) 20 December 1960 cited in the application see column 1, line 36 - column 2, line 13; claims 1,5,10,11 ---	1-3, 7, 10, 11, 16
A	EP,A,0 220 676 (SUDDEUTSCHE ZUCKER-AG) 6 May 1987 see page 3, line 1 - page 4, line 6; claims 1,3 ---	1-3, 8-10, 12-14, 16
-/-		
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
24 JANUARY 1992	- 6. 02. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	SERBETSOGLU A. <i>[Signature]</i>	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,4 721 580 (E.P. GOSSELINK) 26 January 1988 cited in the application see column 21, line 27 - column 25, line 46; claims 1,9-17 ---	1,4, 10-12
A	EP,A,0 264 615 (HENKEL) 27 Apr11 1988 see page 5, line 1 - line 37; claims 1,5 ---	1,2,4, 10,11

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9106980
SA 51982**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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		JP-A- 63270534	08-11-88
		US-A- 5009814	23-04-91

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		CH-A- 359503	
		DE-B- 1072347	
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